PHOTOCHEMICAL REACTIONS

of

TITANIUM DIOXIDE

THESIS

presented for the degree of Doctor of Philosophy

by

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1966.

To my Parents

CONTENTS

Part 1

INTRODUCTION

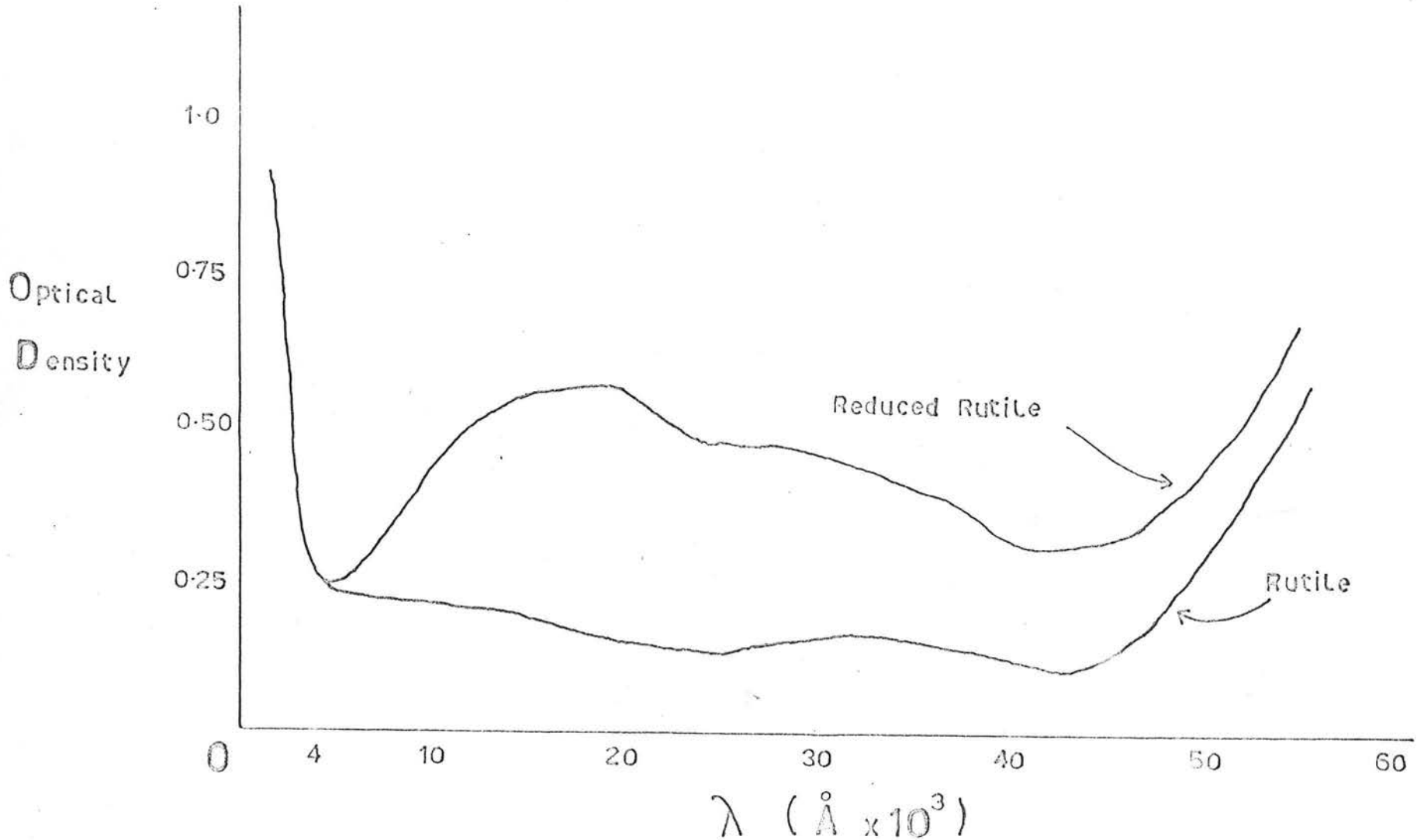

Optical
Density
1·0
0·75
0·50
0·25
0
4
10
20
30
40
50
60
λ (Å x10³)
Reduced Rutile
Rutile

Fig 1

INTRODUCTION

Study of the action of light on titanium dioxide may be regarded as part of the more general problem of the essential nature of semiconducting oxides. Many other investigations were, however, additionally stimulated by the discovery (1) that the photochemical activity of the oxide was related to certain harmful properties displayed by it when contained in industrial preparations of paints and fibres. It is proposed here to deal only briefly with this aspect of its properties, and a fuller account of the historical development of research in this field can be had elsewhere (2, 3, 4).

Originally, the incorporation of TiO_2 in paints and fibres was due to its exceptionally high light-reflecting power. However, exposure of such material to sun-light was found to result in photo-degradative reactions known technically as "chalking" (of paints) and "tendering" (of fibres).

It was established (5, 6, 7) that TiO_2 absorbs in the ultra-violet with a fairly sharp edge at ca. 4000 Å (Fig. 1), and the scheme proposed by Jacobsen (1) to account for the photo-degradations was

$$TiO_2 + \text{vehicle} \xrightarrow[\text{Dark}]{h\upsilon\ (\lambda < 4000\text{Å})} Ti_2O_3 + \text{oxidised vehicle}$$

Weyl and Forland (8) considered the oxidations to proceed via a photolysis mechanism involving the liberation of atomic oxygen from the surface. Earlier attempts made by Goodeve (9) to detect O_2 - liberation from TiO_2 illuminated in vacuo were unsuccesful, however, and it was shown by Egerton (10) that the photo-decompositions occurred only in the presence of

gaseous oxygen. The important discovery was then made by MacKenzie (11) that illumination of the oxide in an O_2 atmosphere led to an uptake of gas by the solid. This photo-adsorbed oxygen is now believed to be the reactive species in such instances (12).

Since MacKenzie's discovery, this and many other photo-adsorption and reaction processes on TiO_2 have been extensively investigated by a number of researchers. For reference purposes, therefore, it will be of value to present here a short list of the more important systems which have been examined, especially those relevant to the present work.

(1) Photoadsorption of O_2 :- (2, 3, 4, 11, 13, 14 - 19).

(2) Other adsorptions :- NO(2, 3, 14) ; NH_3(3, 14) ; H_2O (3, 4, 19-21, 62)
CO (2, 19, 22) ; CO_2 (19, 22) ; N_2O_4(23) ; H_2 (2, 13, 24, 25)
C_2H_4 and C_3H_6 (4, 15)

(3) Photoreactions :- $TiO_2 + O_2 +$ (a) NH_3 (3, 14, 26, 27)
(b) Carbohydrates (17, 28, 29)
(c) C_2H_4 and C_3H_6 (4, 15) (d) H_2O (3, 14)
$TiO_2 + AgNO_3$ (30, 31, 32)

It is the aim of this work to verify results previously obtained (4) for the unsaturated hydrocarbon/TiO_2 system, and to extend the investigations in such a way as to throw more light on the adsorption and reaction mechanisms involved.

In the following section, a short review will be made of available information on the physical and photochemical properties of TiO_2. Particular attention will be paid to the electronic structure of the solid, and to the physical nature of the surface, since such factors are of prime importance in any consideration of adsorption processes.

I Photo-sorption on Semi-conductors

Photo-ad and de-sorptions have been reported as occurring in a large number of systems (e.g. 2, 3, 13, 25, 33-36).

In its simplest form, the effect of light of a suitable wave-length on an n-type semiconductor, is to excite electrons, from donor impurity levels to the conduction band. Schwab (37) thus reasons that illumination, increasing the concentration of electrons in the conduction band, should promote the adsorption of electron-acceptors such as O_2, but should inhibit the adsorption of electron-donors such as hydrogen. Gray and Savage (38), however, consider the possibility of electron-transfer taking place at the impurity levels. Here, illumination produces positive holes so that the adsorption of electron-donors should be enhanced, but electron-acceptors should not be photoadsorbed.

Experimental evidence, however, suggests that illumination may promote the adsorption of both acceptors and donors (e.g. 4, 24, 19). Presumably, electron-transfer may take place either in the conduction band, or at impurity levels, depending on the electronic arrangement of both adsorbent

and adsorbate.

It should be noted here. that the surface of a solid may represent a gross deviation from the bulk structure, e. g. a p-type layer may occur at the surface of a solid with n-type bulk properties (23). Surface electronic states have been proposed by Shockley (39). Further, solid-surfaces are generally not "clean", but carry adsorbed impurities e. g. it is known that TiO_2 has water molecules adsorbed on the surface. These are considered to induce a positive surface charge (40) in opposition to the negative charge expected for the free surface.

(II) Structure of Titanium Dioxide

Titanium dioxide exists in three crystal forms - rutile (tetragonal), anatase (tetragonal prismatic) and brookite (rhombic), the latter being a rare variety. Rutile has been stated to be the only stable modification, anatase and brookite being unstable transition forms (41). Formally, in both rutile and anatase, a central Ti^{4+} ion is surrounded by $6 O^{2-}$ ions to form a slightly distorted octahedron. The binding, however, is predominantly covalent, as is indicated by the low solubilities in polar solvents, and the figure 43% ionic character for the Ti - 0 bond has been proposed (42).

X-ray powder photographs of TiO_2 samples show very diffuse diffraction bands, suggesting a dislocated and disordered lattice (43 and 3), and the rutile structure or "TiO_2 phase" can exist as TiO_2 ..... $TiO_{1.95}$ (44). Originally, this non-stoichiometry was thought to be due simply to oxygen-defects, but the possibility of interstitial titanium ions was shown by

Hurlen (45) from geometric considerations. There is further strong supporting evidence for the presence of interstitial Ti^{3+} (46, 47).

Electronic Structure

Pure, stoichiometric TiO_2 should, on the basis of band theory, be an insulator with an energy-gap, Eg $\sim$ 3-4 e. v. . Electrical data, however, show rutile to be an n-type semiconductor, the current being carried by quasi-free electrons produced from non-stoichiometric defect centres (5, 48, 49, 45). The non-stoichiometry is associated with oxygen-deficiency, as is evidenced by the rise in conductivity of reduced rutile (42).

Thus, oxygen vacancies and/or titanium interstitials, give rise to imperfection centres plus associated electrons, these centres having ionisation energies. Ed $<$ Eg. Such donor sites may be non-interacting, and therefore, H - like, or interaction may occur with overlapping of wave-functions, leading to the formation of a donor band.

The magnetic susceptibility results of Ehrlich (50) indicate the presence in non-stoichiometric rutile of a donor band approximately 0. 04 e. v. wide, and probably lying ca. 0. 1 e. v. below the conduction band. However, the evidence for such a band is not conclusive, and other work (4) suggests the donors to be localised, and non-interacting.

Conductivity measurements suggest Eg = 3-4 e. v. whereas optical adsorption and photoconductivity results lead to Eg = 2. 8 - 3. 1 e. v.

The photoconductivity of TiO_2 shows a maximum in the vicinity of the

optical absorption edge (5, 6), at 0.4. μ (3.06 e.v.), and Cronemeyer (5, 6) regards this as due to a fundamental lattice absorption involving a transition from the valence to the conduction band. On this basis, therefore, Eg = 3.06 e.v. Further, this author places oxygen-vacancy levels at 0.75 and 1.18 e.v. below the conduction band (51).

Breckenridge and Hosler (52), however, regard the 0.4 μ edge as due to a transition between oxygen-vacancy levels and the conduction band. They assume the Franck-Condon principle to apply for solid state transitions and, following Mott and Gurney (53), take ΔE(optical) / ΔE(thermal) = 5.1 Thus, on this basis, Ed = 3.06/5.1 = 0.62 e.v. These authors further consider that direct transition from the valence to the conduction band should occur optically near 18 e.v., this being the normal region for intrinsic absorption in transparent oxides (53).

Bevan, Dawes and Ford (54) examined the spectra of rutile and anatase in the quartz ultra-violet, and, observing absorption maxima in the region 0.2 - 0.3μ, produce evidence to support the hypothesis that these absorptions are associated with electron-transfer from an oxygen to a titanium ion.

Nature of the Donors

Work of Young et al (55) on the e.s.r. spectrum of reduced, and pre-irradiated rutile, is interpreted by Frederikse (46) as suggesting the impurity levels to be due to electrons sited on titanium ions. Similar work by

Chester (47) on reduced rutile led this author to postulate the existence of one or all of :-

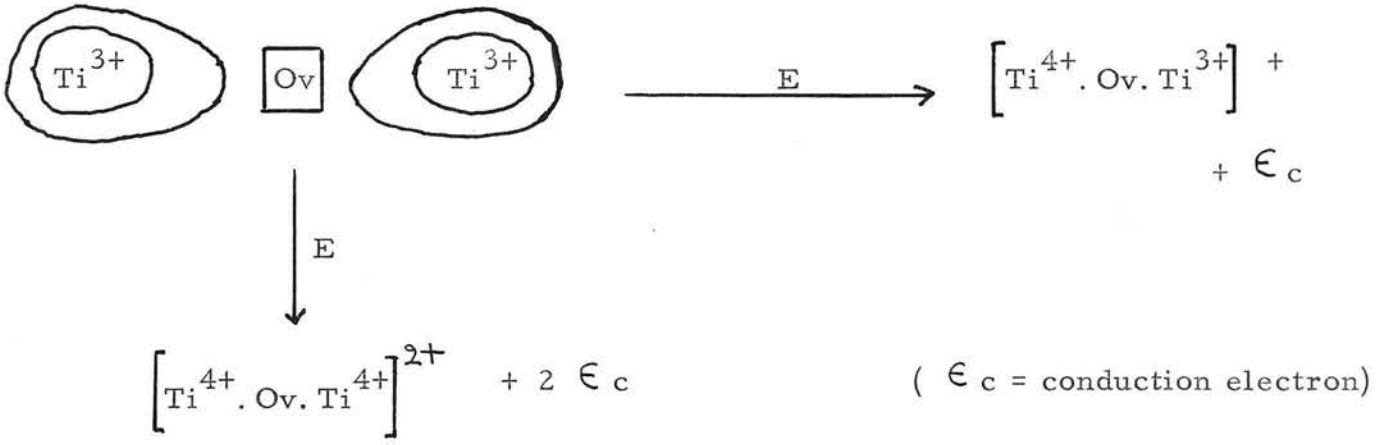
(a) Interstitial Ti^{3+}

(b) Ti^{3+} on a site perturbed by an O^{2-} - vacancy.

(c) An unidentified centre due to H_2 - incorporation within the lattice.

Chester considers the possibility of a polaron-band, while Frederikse (46) considers room-temperature conduction as due to bare electrons excited to the conduction band from polaron states associated with Ti^{3+} ions. Previously, Cronemeyer and others (6, 8, 52) considered the donor sites to be O^{2-} vacancies associated with neighbouring polarised Ti^{3+} ions.

i. e.



Trapping Levels

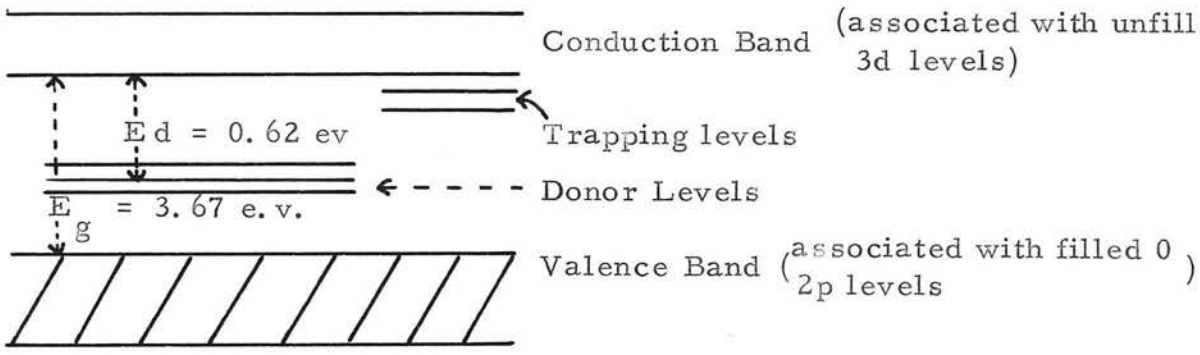
In addition to these donor impurity centres, there is considerable

evidence for the presence of electron-trapping levels in the solid. Such evidence comes from conductivity measurements (4), infra-red absorption (34, 18, 32), dielectric constant measurements before and after X-irradiation (56), and observations of diffuse reflectance spectra (17). The nature of the traps is not known, but they must be associated with imperfection or impurity centres. It has been shown (57) that replacement of some of the titanium ions by foreign ions may greatly reduce the mobility of the free electrons, so that lattice-incorporated impurities may well be responsible for the trapping-action.

More will be said about these traps later.

Summary

There is obviously a degree of uncertainty over the nature, and energy of the defect centres, and even over the value of the energy-gap, Eg. However, the electronic structure of non-stoichiometric TiO_2 would appear to be best presented by the data of Breckenridge and Hosler (52), and the energy-values proposed by these authors are illustrated diagrammatically below.



(III) The TiO_2 Surface

Since we are concerned here primarily with adsorption processes, the nature of the solid-surface is obviously of great importance. Unfortunately little direct information is available. Attempts at electron-diffraction have proved unsuccessful (58), and one of the chief difficulties here and elsewhere concerns the marked dependence of surface properties on sample preparation and pre-treatment. Such differences become particularly apparent when considering adsorption characteristics, and make comparison of results obtained on different samples very difficult.

The results of ortho-para H_2 conversion on TiO_2 (59) suggest the presence on the surface of a number of paramagnetic centres which are also the cause of colouring in reduced rutile. This has been confirmed by Gray et al (48), using magnetic susceptibility measurements, who also found evidence for a high concentration of Ti^{3+} defects near the surface.

The evidence for the existence of electron-traps has been mentioned in the previous section. The results of several workers suggest that the traps must be located at, or near to, the surface. Thus there is an apparent association of electrons in these trapping levels with adsorbed oxygen (18, 4, 17), and with adsorbed silver ions (32). In the latter investigation, Clark and Vondjidis assigned electronic energy levels to the system localised (i. e. trapped) electron - Ag ranging from ca. 0. 14 e. v. to ca. 0. 62 e. v. below the conduction band. It may be of significance to note here that 0. 62 e. v.

is the same value as that proposed by Breckenridge and Hosler for the transition from oxygen vacancy levels to the conduction band (i. e. Ed).

When considering the defect structure of the surface it must be remembered that adsorbed impurities may also be present. Samples used in the present investigations, for example, were prepared by precipitation in NaCl solution, with subsequent neutralisation by NaOH. These samples must, therefore, carry surface-sorbed Na^+, Cl^- and OH^- ions; in addition to any other impurities present in the original reactants.

One aspect of the TiO_2 surface which has received particular attention is that of adsorbed water. Since there is increasing evidence (2, 3, 4, 60) of some form of relationship between this surface water and the photo-properties of the oxide, it is necessary to consider the available information on its nature and properties.

The Hydrated Surface

"Dry" TiO_2 surfaces have a high capacity for water-adsorption, and coverages may be greatly in excess of a monolayer (20, 61). Thus, preparation of the oxide by hydrolysis of titanium salts leaves the TiO_2 in a high state of hydration (3, 62).

Gregg (62) states that although most of this H_2O is lost below $500^{\circ}C.$, a small portion is retained by the solid, and is desorbed only at temperatures $\sim 700^{\circ}$. This is in the region of the Tamman temperature, and Gregg considers this to indicate that the major portion of the H_2O is held on the

surface, and not within the lattice.

The energies of the water-surface bonds are considered (62, 20) to lie within a broad spectrum of values, but the results of Latty (63) indicate a maximum rate of dehydration near 170°C. Asher and Gregg (20) suggest that water expelled (a) below 100°, is molecular in nature, (b) between 100 and 300° is hydrogen-bonded, and (c) above 300° is present as OH groups on the surface.

The infra-red results of Yates (22) show that evacuation at ca. 150° leaves some molecular H_2O, but that only hydroxyl groups remain after evacuation at ca. 350°. Similarly, Bews (17) has observed a broad absorption band at ca. 3,200 cm^{-1}, on samples evacuated at room temperature, which he interprets as due to hydrogen-bonded molecular H_2O aggregates. Yates has made the further observation that apparently two different types of surface hydroxyl occur on anatase, whereas only one type is present in rutile. Rather different results have been obtained by Lewis and Parfitt (61) however, who observe two hydroxyl stretching frequencies in rutile at 350°, which are replaced by one higher-energy band, at 450°C. One possible explanation of these three frequencies is that they are due to isolated OH groups on energetically different crystallographic planes. Such evidence of surface heterogeneity of oxides has been discussed by Taylor and Liang (64).

MacLean (3, 14) has shown O_2 -photoadsorption to alter the binding of water with the surface, the uptake of 1 mole of O_2 resulting in the liberation after pumping, of 2 moles of H_2O. However, the results of McLintock (4)

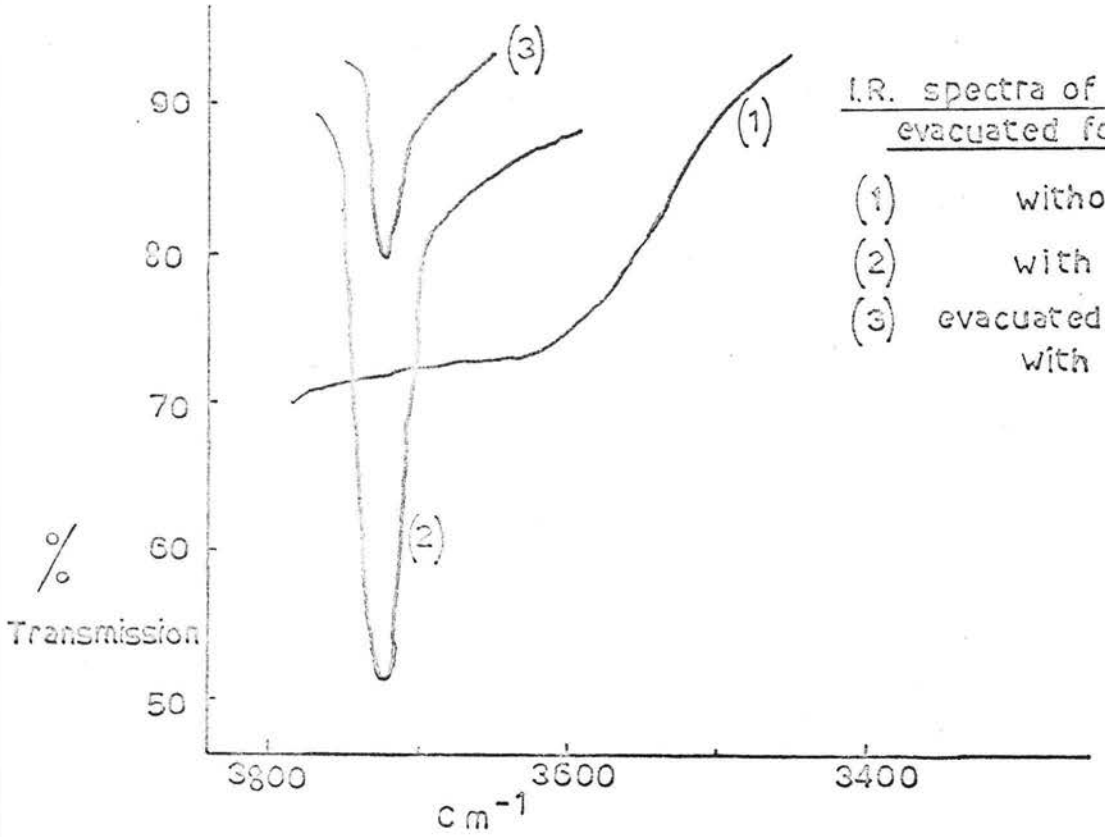

I.R. spectra of rutile discs
evacuated for 20 hrs. at 450°
(1) without O_2 treatment
(2) with " "
(3) evacuated for 2½ hrs. at 610°
with O_2 treatment
(1)
(2)
(3)
90
80
70
60
50
% Transmission
3800
3600
3400
cm⁻¹

Fig 2

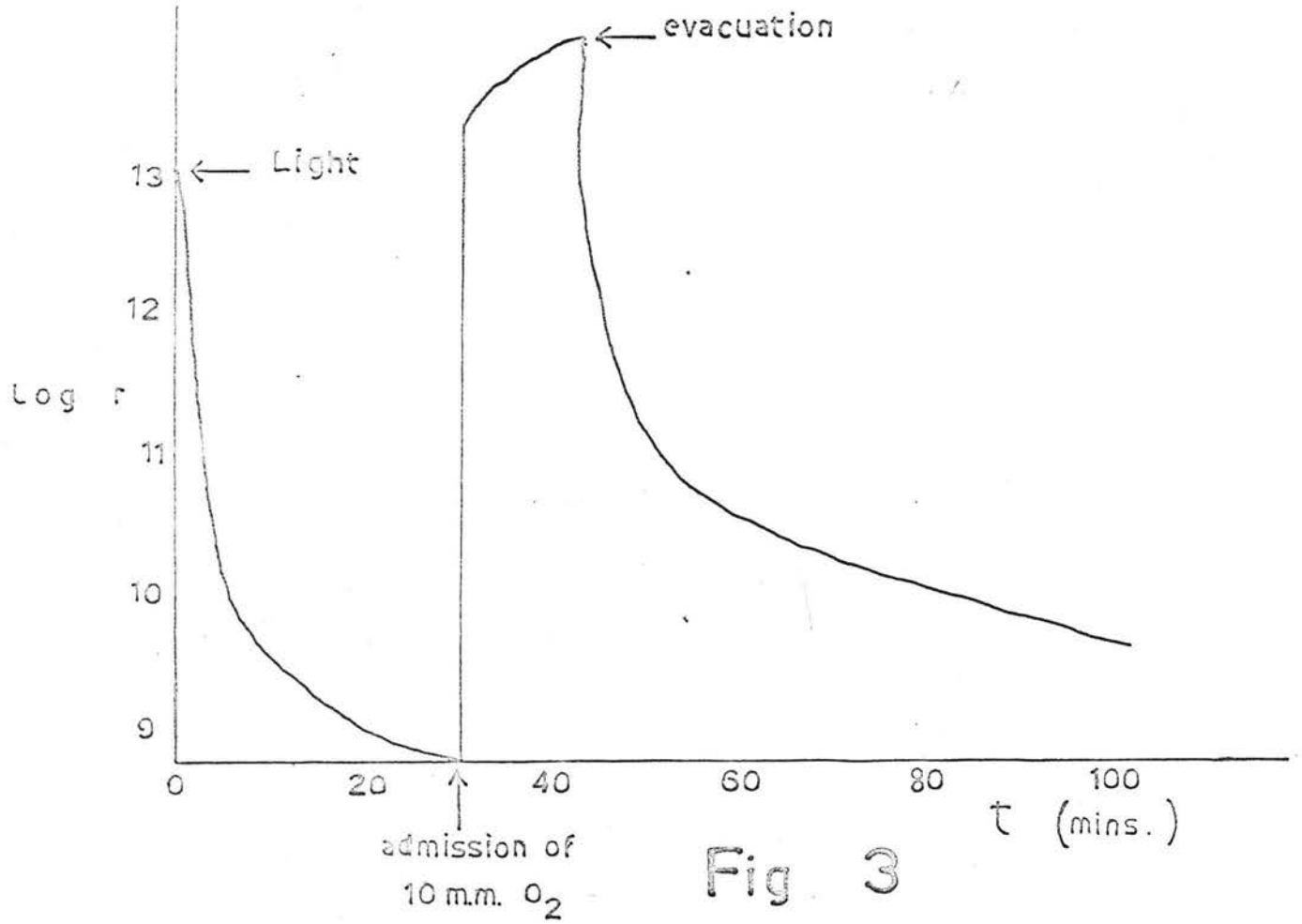

evacuation
Light
13
12
11
10
9
Log r
0
20
40
60
80
100
t (mins.)
admission of
10 m.m. O_2

Fig 3

suggest that surface H_2O or OH groups are not themselves sites for O_2 - photo-adsorption, and the idea is proposed that only water adjacent to photoadsorption sites is displaced. In this connection, it is interesting to note that O_2 - treatment of rutile samples, following a high-temperature evacuation, has a marked effect on the OH region of the I. R. spectrum (61.) The spectra of samples not O_2 - treated after evacuation at temperatures $> 250^{\circ}$, showed the hydroxyl - absorptions to be perturbed in a manner suggestive of hydrogen-bonding. O_2 - treatment at the temperature used for the evacuation removed this perturbation, while at the same time restoring the original white colour lost during heating. (see Fig. 2). The discolouration of rutile heated in vacuo has been associated with a surface-reduction process (65, 66), and it has been shown that this reduction and subsequent O_2 - treatment has a marked influence on other surface properties such as heats of wetting (65).

Measurement of resistance changes of TiO_2 pellets (4) accompanying H_2O-sorption at room temperature, reveals the presence of at least two types of adsorbed H_2O. These may be adsorbed simultaneously, or one type may revert slowly to the other. McLintock makes the interpretation that water is initially adsorbed as the positive species (H_2O^+, this surface species then slowly reverting to OH^-

i. e.

The further observation is made that the initially adsorbed H_2O has the effect of suppressing the photoconductance of the solid, and it is suggested that either

(*) The electrons donated by the H_2O are sufficient to fill the available conduction levels.

or

(2) H_2O is adsorbed at sites which normally act as donors of photo-electrons, thus destroying the photoactivity of these sites in some way.

(IV) Photo-sorption on Titanium Dioxide

As has been stated (see Introduction), MacKenzie (11) was the first to show that illumination ($\lambda < 4000$ Å) of TiO_2 films in an O_2 atmosphere led to an uptake of gas by the solid. This work was extended by Kennedy (2), who examined the characteristics of the uptake on variously prepared and pre-treated samples. The amount, and rate, of the uptake were found to vary with the method of preparation and pre-treatment. Rutile was shown to have a smaller photoadsorptive capacity than anatase.

The rate of the photouptake on any one sample was found to depend on (1) the O_2 - pressure. (2) the wave-length of the light used (3) the light-intensity, (4) the coverage, θ, and (5) the temperature, in the following manner:-

(1) At any stage of the uptake, the rate of uptake, $d\Delta p/dt$, was found to obey the relationship

$$\frac{d\Delta p}{dt} = \text{const} \times \theta$$

where $\theta/1-\theta = A.P.^{\frac{1}{2}}$ (p = gas pressure, A = const.)

This equation is of the Langmuir type for dissociative adsorption, and suggests that the rate is determined by the concentration of oxygen atoms (or ions) on the surface.

(2) No light of $\lambda < 3,200$ Å was passed by the glass of the apparatus. Rates were studied using monochromatic light of λ 3650, 4050 and 4360 Å, and the 3650 Å line was shown to be most efficient, light of $\lambda >$ 4000 Å having little effect on the uptake. The percentage of light transmitted by the TiO_2 film was also lowest with light of λ 3650 Å.

(3) The rate was found to be directly proportional to the intensity of 3650 Å light absorbed by the dioxide

i, e.

$$\frac{d\Delta p}{dt} = \text{const. I abs}$$

(4) The rate of uptake was shown to fall off with increasing coverage, θ. The kinetics of the process will be discussed separately.

(5) The reaction-rate was found by MacKenzie (11) to be subject to a temperature coefficient of ca. +5 K cals $mole^{-1}$. The presumed Langmuir dissociative adsorption will be temperature-dependent, but it is also possible that this effect is associated with surface diffusion (2) (see also Sec. VII)

The above results were verified by MacLean (3), who further showed the O_2 -uptake to be attended by the production of water, in the molar ratio 2 : 1. This result has been confirmed (19) for TiO_2 films initially evacuated at room-temperature, but with evacuation at higher temperatures this ratio no longer seems to hold. Only trace amounts of H_2O are produced after an initial evacuation at $170^{\circ}C$. (4).

Kinetics of the O_2 photouptake

Different kinetics have been reported by different investigators. Kennedy (2), and Ritchie et al (13) report a "parabolic" relationship to hold over the initial stages, when this uptake, 'Δp', at time 't' could be represented by

$$(\Delta p + p')^2 = kt + p'^2 \qquad (p', k \text{ const.}; p' \text{ small})$$

In the later stages, an exponential law was found to apply

$$\Delta p_{\infty} - \Delta p = \Delta p_{\infty} \cdot e^{-kt}$$

or

$$\frac{d\Delta p}{dt} = k \ (\Delta p_{\infty} - \Delta p)$$

This allowed extrapolation to zero rate, in order to derive the uptake at infinity, Δp_{∞} ($\sim$ 200 μmoles g^{-1})

MacLean (3), however, found the Elovich rate law to hold over the initial stages.

$$\text{i.e.} \quad \frac{d\Delta p}{dt} = a.e.^{-b\Delta p} \qquad (a, b \text{ const})$$

this being succeeded by an exponential expression similar to that of

Kennedy.

More recently, McLintock (4) and Bews (17) report the kinetics to be again parabolic initially.

i. e. $$(\Delta p + p')^2 = kt + p'^2$$

and, finally, Elovich in nature.

It is apparent, from the above that there is here further evidence of the influence of sample preparation on the subsequent adsorption characteristics.

Adsorption of Unsaturated Hydrocarbons

The photosorption, and reaction with 0_2 at 25°C, of ethylene and propylene on $Ti0_2$ surfaces (previously evacuated at 170°C) have been examined by McLintock (4).

Neither gas was found to adsorb in the 'dark' (i. e. in the absence of light of $\lambda < 4000$ Å), but C_2H_4 photoadsorbed in a manner analogous with that of 0_2, the amounts taken up generally being less ($\sim$ 20 μmoles g^{-1} Cf. 40-50 μmoles g^{-1}). C_3H_6, however, did not photoadsorb unless the surface was pre-treated with photoadsorbed 0_2. A high temperature evacuation following such a C_3H_6 uptake at 25°C resulted in the recovery of small amoun ts of CO_2, H_2O and HCHO. In a similar way, the uptake of C_2H_4 was enhanced by pre-sorbed 0_2, though reaction products were not obtained in this case.

The Kinetics of the uptake of both gases were found to consist of an initial section where a parabolic expression was obeyed.

$$(\Delta p + p')^2 = kt + p'^2$$

which was succeeded by an Elovich-type expression

$$\frac{d\,\Delta p}{dt} = a.\,e.^{-b\,\Delta p}$$

The Elovich section was found sometimes to be 'compound' - i. e. a plot of $\log \frac{d\,\Delta p}{dt}$ vs. Δp giving more than one straight line. Up to three Elovich sub-sections were encountered in one photosorption, each having its own values of 'a' and 'b'.

Unlike 0_2, the adsorption of neither hydrocarbon appeared to affect the water-surface bond, and McLintock draws the conclusion that the sites for 0_2-adsorption differ from, or are not at all available for olefin - sorption.

Extent, and Reversibility of the Uptakes

(A) Oxygen

As has been said earlier, the amount of 0_2 taken up by a $Ti0_2$ sample depends on the method of preparation, and pre-treatment of the sample. It has been shown (2) that laboratory prepared samples exhibit more adsorptive activity than commercial grade samples, that anatase is generally more active than rutile, and that chromium-treated samples are less active than the corresponding untreated samples. The uptakes varied from ca. 200 μ moles g^{-1} for laboratory-prepared samples to, ca. 10 μ moles g^{-1} for technical-grade samples. It was found, further, that thorough drying of the $Ti0_2$ powders (evacuation at temperatures $\sim$ 150-200°) resulted in a slight increase in activity, whereas treatment in an oxidising or reducing atmosphere (at 400°C) had little effect on the subsequent 0_2-uptake. Treatment of the powder in hydrogen at 800°C resulted in a large decrease in activity. This result is of particular interest since such a treatment produced a definite deficiency of oxygen in the $Ti0_2$, accompanied by the evolution of H_2O. The result may, however, be associated entirely with the temperature of treatment. Though samples prepared at room temperature have high surface areas ($\sim$ 100-300 $m^2 g^{-1}$), strong heating leads to sintering, and the surface area as measured by N_2 sorption becomes considerably smaller (62).

It has been shown (17) that the 0_2-uptake is increased by the presence

of oxidisable material (e. g. carbohydrates) on the surface, up to a point where a blocking effect is encountered. An analogy may be drawn between this and the increase in uptake resulting from the pre-sorption of unsaturated hydrocarbons (4).

The other factors influencing the extent of 0_2-uptake (e. g. gas pressure, light intensity) have already been mentioned.

It now seems established that the eventual photo-uptake is irreversible, evidence coming from conductivity measurements (3, 4, 15), and from the failure of attempts to recover photoadsorbed 0_2 by evacuation (4). It has been reported, however, that such an evacuation leads to a partial renewal of adsorptive activity.(2, 4). This is attributed by Kennedy to the removal of binding liquid blocking adsorption sites (2).

The situation in the initial stages of the uptake is not yet clear. Conductivity measurements (16, 4), however, suggest an initial, very small, reversible adsorption in the dark. Further, the photo-uptake is considered also to be initially reversible, prolonged illumination leading to the irreversibly chemisorbed species.

(B) Olefins

Except as given above, no detailed studies have been made on the effect of pretreatment of the surface on the extent of the hydrocarbon uptakes.

The adsorptions are again regarded as essentially irreversible, though it is stated (4) that very small amounts of photo-adsorbed propylene were

recovered by thermal evacuation. However, since the sorption of these olefins has little or no effect on the conductivity of the solid (4, 15) it is impossible to say whether the processes are initially reversible or not. Intermediate evacuation at elevated temperatures (ca. 170°) did give rise to a partial renewal of adsorptive capacity without, however, any detectable desorption taking place. Films pre-treated at 170° and 250° did not differ in adsorptive capacity whereas a 250° evacuation following a C_2H_4 uptake is stated to be the more effective in renewing activity. This is taken by McLintock as evidence that the thermal treatment regenerates original adsorption sites, (by, for example, causing a surface migration process), rather than creating new ones.

(V) The Photo-oxidation of Ethylene and Propylene

When O_2 was taken up by a TiO_2 film previously treated with either olefin, subsequent evacuation at elevated temperatures resulted in the recovery of small amounts of CO_2, H_2O and HCHO, whereas films untreated with hydrocarbon gave only CO_2 and H_2O in smaller amounts (4). Surprisingly, the reverse did not appear to hold, i.e. the uptake of C_2H_4 on O_2-treated films did not give rise to detectable oxidation products; in the case of C_3H_6, trace amounts of C_3H_6, CO_2, H_2O and HCHO were recovered.

When a film was illuminated in a hydrocarbon-oxygen atmosphere, however, very large and rapid pressure decreases took place, the uptake being accompanied by the production, again of CO_2, H_2O and, sometimes, HCHO, these species being largely retained by the surface and only recovered by thermal evacuation. In the case of C_3H_6-O_2 mixtures, a small dark uptake was reported, followed by a faster and more extensive photo-uptake, similar to that of C_2H_4-O_2 mixtures.

The stoichiometric equations proposed by McLintock (4) for the oxidation of ethylene and propylene are, respectively :-

$$C_2H_4 + 3O_2 \longrightarrow 2\,CO_2 + 2\,H_2O$$

and

$$C_3H_6 + {}^5/_2\,O_2 \longrightarrow CO_2 + H_2O + 2\,HCHO$$

Two points are worthy of notice here :-

(1) The amounts of H_2O and HCHO recovered were always lower, and frequently the amount of O_2 used up was greater, than ex-

pected from the above equations. This was attributed to retention of products by the surface, and adsorption of excess 0_2 not utilised in the photo-reaction.

(2) A partial oxidation of C_2H_4 to HCH0 was encountered on one occasion, despite the presence of a large initial excess of 0_2.

(VI) The Photoconductivity of $Ti0_2$

The phenomenon of photoconductivity is observed in many semiconductors (e.g. 3-6, 67-70), and is due to the elevation of electrons from filled to unfilled energy-levels in the solid, the necessary energy coming from the absorbed quanta. Such transitions give rise to an increase in the density of charge-carriers - electrons in the conduction band in the case of n-type semiconductors, and positive holes in the valence band for p-type semiconductors. Both processes may occur in solids which possess both donor and acceptor levels, or in solids which possess impurity bands .... e.g. irradiation with a suitable wave-length, of an n-type semiconductor having a donor band, could give rise to conduction both by electrons in the conduction band, and by positive holes in the donor band. The same situation would, of course, arise if photoconductivity resulted from direct transition between the valence and conduction bands. However, the normal region for such intrinsic absorption in oxides lies in the far ultra-violet (53).

Titanium dioxide is an n-type semiconductor (5, 48, 49), having a dark in vacuo resistance $\sim 10^{12}\ \Omega$ cm at room temperature. Illumination with

light of $\lambda < 4000$ Å in vacuo, however, causes a large decrease in resistance, the rate of decrease falling off parabolically with time of illumination. The final value of the light resistance is then $\sim 10^8$ Ω cm (4, 13). That the effect is the genuine result of absorption of light is shown by the dependence on wave-length, a conductivity peak being shown in the region of the absorption edge (5, 6).

Cessation of irradiation leads to a slow decay in conductance, a steady value being attained only after 2-3 days (4), and this resistance value always being less than the original (dark) resistance. Similar results are reported by Kennedy (16) who, however, states that the photoconduction decay is rapid and complete if the dioxide sample is held at 120° following a short period of illumination.

Such results are compatible with the idea of surface traps arranged at varying depths in the solid (see Sec. II & III). The slow decay of photoconductance would then be due to a thermal trap-emptying process, and would be expected to be accelerated by heating (3, 4).

Since chemisorption involves the transfer of electrons between adsorbent and adsorbate, it is obvious that the study of conductivity changes accompanying adsorption processes would be of particular value. Such studies have been made on TiO_2 in conjunction with the uptake of O_2 (3, 4, 13, 15, 16), NH_3 (3), C_2H_4, C_3H_6 and H_2O (4, 15).

(A) Oxygen

The admission of 0_2 to an illuminated $Ti0_2$ pellet has the effect of destroying the initially developed photocurrent, the new resistance of the pellet sometimes exceeding the original dark resistance (4) (see Fig. 3). In a similar way, the presence of 0_2 inhibits the development of photoconductivity when the $Ti0_2/0_2$ system is illuminated, though a small photocurrent is in fact developed. Several immediate conclusions may be drawn :-

(1) The photoconductance is a surface effect - this is to be expected since only surface particles will be exposed to the incident radiation.

(2) As previously supposed, the adsorption of 0_2 involves transfer of electrons from the solid to the gaseous, or physically sorbed oxygen.

And, following from this,

(3) The charge carriers must be electrons, and these must be few in number, since the presence of only a very small amount of adsorbed oxygen results in the complete destruction of photoconductance. For the same reason, there can be no p-type contribution to the photocurrent.

This last observation is taken by McLintock as suggesting that the effect of illumination is to elevate electrons to the conduction band from discrete donor levels rather than from a donor band, or the valence band.

The effect of 0_2 in the dark is stated by Ritchie et al (13) to be a small decrease in resistance, reversible by evacuation. Kennedy, however, finds the opposite to be true (16), and, similarly, McLintock (4) finds that the admission of 0_2 to an evacuated $Ti0_2$ pellet gives rise to an increase in the dark resistance, this effect not being reversed by evacuation.

All the workers agree, however, that prolonged illumination in 0_2 leads to an irreversible destruction of photoconductance, this being taken as evidence of the irreversible nature of the sorbed oxygen.

It has been shown, on the other hand (4), that the original photoconductivity of a sample may be restored following 0_2-treatment, if the gas is pumped out immediately after the resistance-increase (see Fig. 3). This reversal of resistance-increase is shown to be a relatively slow process similar to the development of photoconductance, and isolation from the pumps caused neither any discontinuity in the fall of resistance, nor any pressure increase measurable by Pirani gauge. It is concluded that the 0_2 photosorption is reversible at this stage, the slow resistance decrease presumably again resulting from a trap-emptying process.

(B) Water

Small fluctuations in conductivity observed during the course of such studies involving 0_2, were attributed to changes in the amount, or character, of surface water. It has been mentioned earlier (Secs. III, IV) that the adsorption of 0_2 does affect the surface-H_20 bond and, accordingly, the effect

of adsorbing various quantities of H_2O on the dark, and photo-conductivity of TiO_2, was examined by McLintock (4).

The admission of small pressures ($\sim$ 1 mm.) of H_2O vapour was found to cause resistance decreases of the same order as those due to illumination. Generally, an initial fast decrease in resistance was succeeded by a slow increase, but the final value of the resistance was always less than the initial vacuum value. These resistance changes were reversed by evacuation, indicating a weak surface-water bond under these conditions. Similarly, Gregg (62) considers the sorption isotherms of H_2O vapour at 25° C. to reveal the presence of a type of binding intermediate between chemisorption and physisorption. The interpretation made by McLintock of the slow resistance increase is in terms of a slow surface conversion of H_2O^+ to OH^-, involving the localisation of a conduction electron. (see Sec. III).

It was found further that this resistance increase was largely suppressed by the pre-photoadsorption of O_2, this being explained as due to the filling of oxygen vacancies, and the resulting prevention of formation of OH^- in the above scheme.

Illumination following a resistance decrease due to adsorbed H_2O was found to give rise to little further decrease in resistance, i. e. no appreciable photoconductance was developed in the presence of surface water. Again, this has been explained in terms of filling of available conduction levels, or poisoning of photo-electron donor sites (see Sec. III).

(C) Unsaturated Hydrocarbons

The presence of a π -electron system in ethylene and propylene suggests the probability of chemisorption taking place via electron-transfer from the hydrocarbon to the solid, and this mechanism has been proposed for several olefinic adsorption processes on oxides (71, 72). Similarly, from his studies of propylene oxidation on a variety of oxides, Emmett (73) places the activity of these oxides in the order p-type > n-type > i-type. This again suggests the olefin to be the electron-donor in such instances.

It is, then, all the more surprising that McLintock reports (4, 15) no change in photoconductivity when either C_2H_4 or C_3H_6 is admitted to an illuminated TiO_2 pellet. Very small changes were reported in the dark, an initial small decrease in resistance being usually succeeded by a small increase. Such effects were found to be irreproducible, and were attributed to changes in the amount or character of surface water.

(VII) Interpretation of the Uptake Kinetics - Possible Adsorption Mechanisms Involved

Many attempts have been made at formulating adsorption and reaction schemes for the various uptakes, and at correlating these with the observed kinetics. It is proposed here to deal only with the adsorption and reaction of O_2 and the olefins (for NH_3, NO etc. see appropriate references in 'Introduction'), and to treat these topics separately.

A. Oxygen

Though different workers have disagreed on the mathematical nature of the O_2 uptake kinetics, all have found these to be resolvable into at least two sections (see Sec. IV).

It appears established that the initial stages of the uptake may generally be described by a "parabolic" relationship, where the uptake 'q' at time 't' is given by $(q + q_o)^2 = kt + q_o 2$ (q_o const).

It has been proposed (2) that such a relationship may result from a surface diffusion process which is initially rate-determining, and the analogy is drawn between this and Wagner's treatment of the growth of thin oxide layers on metal surfaces (74). In the latter instance an expression similar to the above holds, and is considered to be due to the slow diffusion of oxide ions through the layer.

The existence has been demonstrated (11) of a small, positive temper-

ature coefficient (ca. 5 K cals mole^{-1}) for the 0_2 sorption on $Ti0_2$, and it is possible that this may be associated with an energy of activation for such a diffusion across the surface (2).

The final stages of the 0_2 uptake were found by Kennedy (2) to be best represented by an exponential expression (see Sec. IV).

$$q_{\infty} - q = q_{\infty} . e^{-kt}$$

(where q_{∞} is the experimentally determined uptake at infinity, obtained by extrapolation to zero rate). The overall process of 0_2 adsorption is interpreted in terms of a two-site mechanism. At the first set of sites ('A' sites), supposed to be few in number, the chemisorption is considered to be reversible and dissociative, and to take place in the dark.

i. e.

$$\tfrac{1}{2}\ 0_{2(g)} + A \quad \rightleftharpoons \quad A^{+}0^{-}(s)$$

Illumination is then considered to produce conduction electrons, some of which become trapped at empty 'A' levels, freeing 0^{-} for diffusion

$$A^{+}0^{-} + \epsilon \quad \rightleftharpoons \quad A + 0^{-}$$

The 0^{-} species may then diffuse to the 'B' sites (much greater in number than the "A' sites) where there is rapid combination with the positive holes of the valence band to produce the irreversibly sorbed species

i. e.

$$B\ 0^{-} + \oplus \longrightarrow B^{+}0^{-}$$

As already stated, parabolic kinetics are supposed to obtain while the above diffusion process is rate-determining, and Kennedy considers that exponential kinetics will result when the availability of 'B' Sites becomes the dominant rate-controlling factor. In this connection it is interesting to note that anatase samples, which are photochemically more active than rutile ones, show predominantly exponential uptake curves, while rutile gives only parabolic uptakes. Accordingly, it has been suggested (2) that rutile may possess a much smaller number of 'A' sites than anatase.

The adsorption scheme proposed by McLintock (4, 15) is again in terms of an initial reversible photo-process, succeeded by an irreversible chemisorption involving electron-transfer from sorbent to sorbate. The proposed nature of the surface oxygen, however, differs in that the reversible species is considered to be molecular, the subsequent dissociation process then being irreversible.

i.e. $O_{2(g)} \rightleftharpoons O_{2(s)} \overset{h\upsilon \ \epsilon}{\rightleftharpoons} O_2^-(s)$

and $O_2^- \longrightarrow O^- + O$

or $O_2^- \xrightarrow{\epsilon} O^- + O^-$

On the basis of this scheme, at least two types of photoadsorbed oxygen are evident ..... O_2^- and O^- ..... and McLintock considers that a third form of adsorption is revealed by the small, irreversible dark uptake indicated by his conductivity results (see Sec. VI). Such an adsorption could lead to the same type of surface species as the above, though utilising a different source of electrons.

The kinetics encountered by McLintock were again initially parabolic, but in the later stages the Elovich equation applied.

i.e. $$\frac{dq}{dt} = a.e.^{-bq}$$

It is suggested by this author that Elovich kinetics describe the characteristic property of the process, and that the parabolic expression may have no physical significance, being merely a reflection of a slow attainment of electronic equilibrium under illumination. The proposal is made that the effect of O_2 is the rapid removal of a small number of photo-conduction electrons which are in equilibrium with electrons in trapping levels, and that the subsequent rate of O_2-uptake is governed by the rate of excitation of electrons from such traps to the conduction band. Such a process would require an increasing energy of activation with coverage of negatively charged oxygen ions, and this situation has been stated to give rise to Elovich kinetics (67, 75). It is, in fact, possible to show (76) that the Elovich equation can arise from an Arrhenius-type equation.

$$dq/dt = A.e^{-Ea/RT}$$

if the assumption is made that the energy of activation for chemisorption, Ea, increases linearly with coverage.

The procedure generally adopted in studying the uptake kinetics on TiO_2 has been to irradiate the initially "dark" TiO_2/O_2 system and follow the resulting pressure decreases with time. It might be expected, with the above picture of O_2 uptake in mind, that this situation would, kinetically, differ

from one in which the gas was admitted to the TiO_2 following several hours previous irradiation of the solid in vacuo. Experiments of this type have been carried out (4, 77) with conflicting results. It is stated by McLintock, however, that the general shape of the photouptake curve remains unaltered using this second procedure, and he makes the conclusion that the rate of excitation of electrons from donor levels is approximately the same as that from traps.

A rather different approach to the problem has been made by Bews (17), who investigated the effect of 'pre-treating' the TiO_2 surface with carbohydrates, and with urea. Illumination of such films in O_2 was found to result in an increased uptake of gas, this being accompanied by oxidation of the organic material. Further, the presence of such oxidisable material was found to modify the photouptake kinetics : carbohydrates led to an increase in the rate, duration and extent of the parabolic kinetics, whereas urea modified them to a different form. The relationships derived by Bews led him to postulate the existence on "untreated" TiO_2 of a small amount of some oxidisable entity which required the same mechanism of oxidation as the carbohydrates. Such 'impurity centres' were considered to be oxygen-vancancies, titanium interstitials, or to be due to organic contamination.

A reaction scheme is proposed, whereby "irreversibly adsorbed oxygen" is in part used to oxidise the organic material (or impurity centres) on the surface, and in part occupies adsorption sites.

i. e. $O_{2(g)} \rightleftharpoons O_{2(s)} \rightleftharpoons O_2^-(s) \longrightarrow$ oxygen irreversibly adsorbed

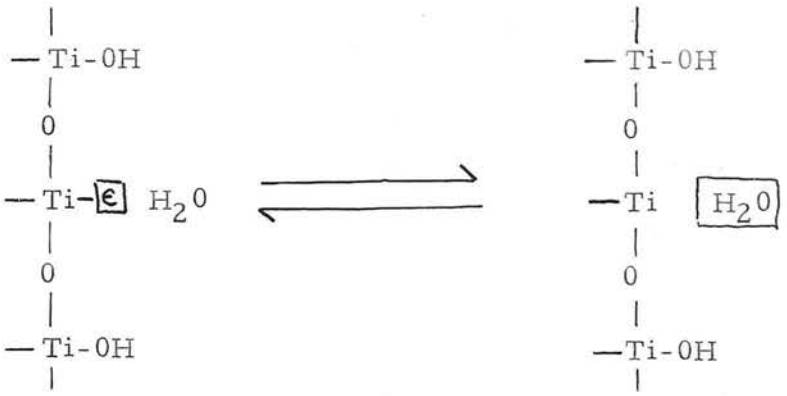
Oxidation site

adsorption site.

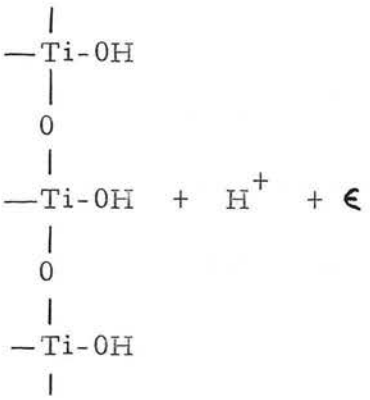
On the assumption that only oxygen occupying 'adsorption sites' (as above) is responsible for retarding the uptake, it is possible on the above basis to explain the increased rate of uptake with increasing weight ratio of sugar to TiO_2. Thus Bews considers that the initial, parabolic process on untreated TiO_2 involves an oxidation reaction with surface impurity centres, and that, when all such centres are oxidised, exponential (Elovich) kinetics will commence. The actual mechanism governing the parabolic kinetics could, again, involve a surface migration of adsorbed oxygen to these centres. Again, the Elovich kinetics are assumed to represent the adsorption process proper, and to be a reflection of the increasing height of the barrier layer formed on the surface with increasing photo-uptake of O_2.

The observation (3) that the photouptake of 'n' moles of O_2 results in the production of '2n' moles of H_2O on films previously evacuated at room-temperature, led MacLean to postulate the existence on the TiO_2 surface of impurity centres of the Lewis-acid type found in SiO_2/Al_2O_3 catalysts(78). Such a centre, on TiO_2, is supposed to be hydroxyl-vacancy in the surface, accommodating an H_2O molecule. In the ground state the free electron associated with the vacancy is formally considered to be accommodated within the 3 d level of a neighbouring Ti^{4+} ion

i.e.



The absorption of a quantum of light of λ = 3650 Å is supposed to cause a transition from this ground state to



The formation of 2 moles of H_2O from 1 mole of adsorbed O_2 can then be represented by

$$O_2 \xrightarrow{2\epsilon} 2O^- \xrightarrow{2H^+} 2OH^-$$

and

$$2OH^- + 2H^+ \xrightarrow{2\epsilon} 2H_2O$$

Thus, four of the above activated sites are utilised in the adsorption of one molecule of O_2 and the production of two molecules of H_2O.

However, it has been shown (4) that films evacuated at higher temperatures (ca. 170°C), and hence carrying less molecular water (see Sec. III), photoadsorb O_2 without releasing H_2O in the molar ratio 2 : 1. In fact, only trace amounts of H_2O are recovered under such conditions, and it is now proposed that the 2 : 1 ratio represents an optimum value (14), and may not

reflect an intrinsic property of the photouptake.

It is, therefore, difficult to correlate such findings with the idea of Lewis-centres representing adsorption sites per se. It is possible, however, that an initial uptake on some other set of sites could be succeeded by a migration to these, or similar sites, followed by reaction and the subsequent production of H_2O. The similarity between such a scheme and that of Bews is striking, and the possibility of a centre associated with surface water representing an "oxidisable entity", presents itself.

This idea, and further evidence for and against the various reaction schemes outlined here, will be discussed later (Discussion).

B. Unsaturated Hydrocarbons

The kinetics of photouptake of C_2H_4 and C_3H_6 have been reported (4) as being of the same form as those of the O_2 uptake (see Sec. IV). The repeated occurrence, in the early stages of uptake, of parabolic kinetics, is taken (4) as further evidence of their electronic origin, since no appreciable diffusion of the bulky hydrocarbon species is considered likely to take place.

It should be noted, however, that a $q^3/2$ vs. t relationship has been reported (77) as being linear over the pre-Elovich stages of some C_2H_4 uptakes and that in these instances this expression was more closely followed than the normal $(q + q_o)^2$ relationship.

Since the conductivity levels of the oxide do not appear to be involved in the hydrocarbon sorptions (see Sec. VI), it has been suggested (4, 15), in

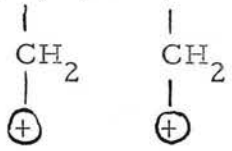
analogy with other work on ZnO (71), that there must be interaction between the hydrocarbons and the holes produced by illumination at donor levels. On this basis, it is again necessary to introduce the concept of surface-traps in order to explain the absence of :-

(a) Photo-desorption of olefin arising from a hole-capture reaction of the type C_2H_4------⊕ ---ϵ---→ C_2H_4

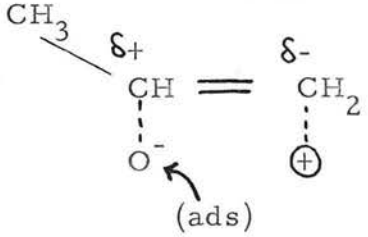
and

(b) Any increase in photoconductivity, which would result from the prevention of recombination of holes and electrons.

The observation (Sec. IV) that no photoadsorption of propylene takes place without the surface being first treated with photoadsorbed oxygen, has led McLintock to conclude that, whereas C_2H_4 will combine with positive holes alone, C_3H_6 further requires the presence of surface O^- species. No direct information is available as to the nature of the surface-hydrocarbon bond, but the forms taken by adsorbed C_2H_4 and C_3H_6 suggested by McLintock (after Wolkenstein), (79) are, respectively



and



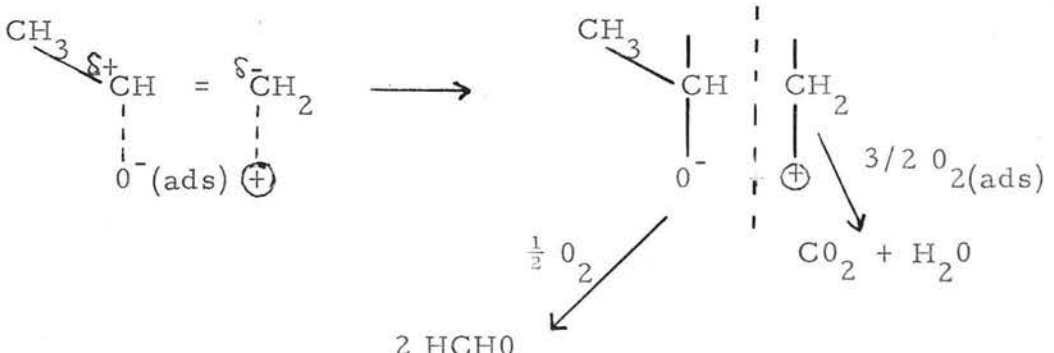
C. <u>The Hydrocarbon Oxidations</u>

C. The Hydrocarbon Oxidations

The stoichiometric equations proposed for the photo-oxidation of ethylene and propylene have been given earlier (Sec.V). On the assumption that the oxidations are surface processes, it is obvious from these equations that several adsorbed oxygen species are involved in reaction with one hydrocarbon molecule. The fact that oxidation is observed to occur only in situations where adsorbed olefin is brought into contact with freshly photoadsorbed O_2 (4), has led McLintock to conclude that it is the initially adsorbed oxygen which is reactive. On the basis of this author's adsorption scheme (see A) it is the reversibly photosorbed O_2^- which is the oxidising species, and such an entity could also be involved in the observed dark uptake of C_3H_6/O_2 mixtures.

The oxidation of C_2H_4 is, then, considered (4) to take place via surface migration of O_2^- to adsorbed species of the type $[-CH_2-\oplus]$ proposed earlier, followed by reaction to produce CO_2 and H_2O. The intermediate in this process is considered to be of the type $[O-CH_2-\text{surface}]$ which is oxidisable, whereas $[CH_2\cdots O^-_{ads}]$ is unoxidisable and responsible for the formation of formaldehyde.

The proposed mechanism of C_3H_6 oxidation can be represented schematically as



CO_2 and H_2O are thus thought to be produced via a mechanism similar to the C_2H_4 oxidation, and similarly HCHO results from the unoxidisible intermediate $\left[CH_2 : : : : O^-_{(ads)} \right]$ as before.

Due to the obvious complexity of the processes, the above mechanistic schemes must be viewed as highly tentative. There is the possibility, for example, of the olefin-oxide being an intermediate. Ethylene and propylene oxide have been reported (4) to adsorb on TiO_2, and to be photo-oxidisable to CO_2, HCHO and H_2O.

Part 2

EXPERIMENTAL

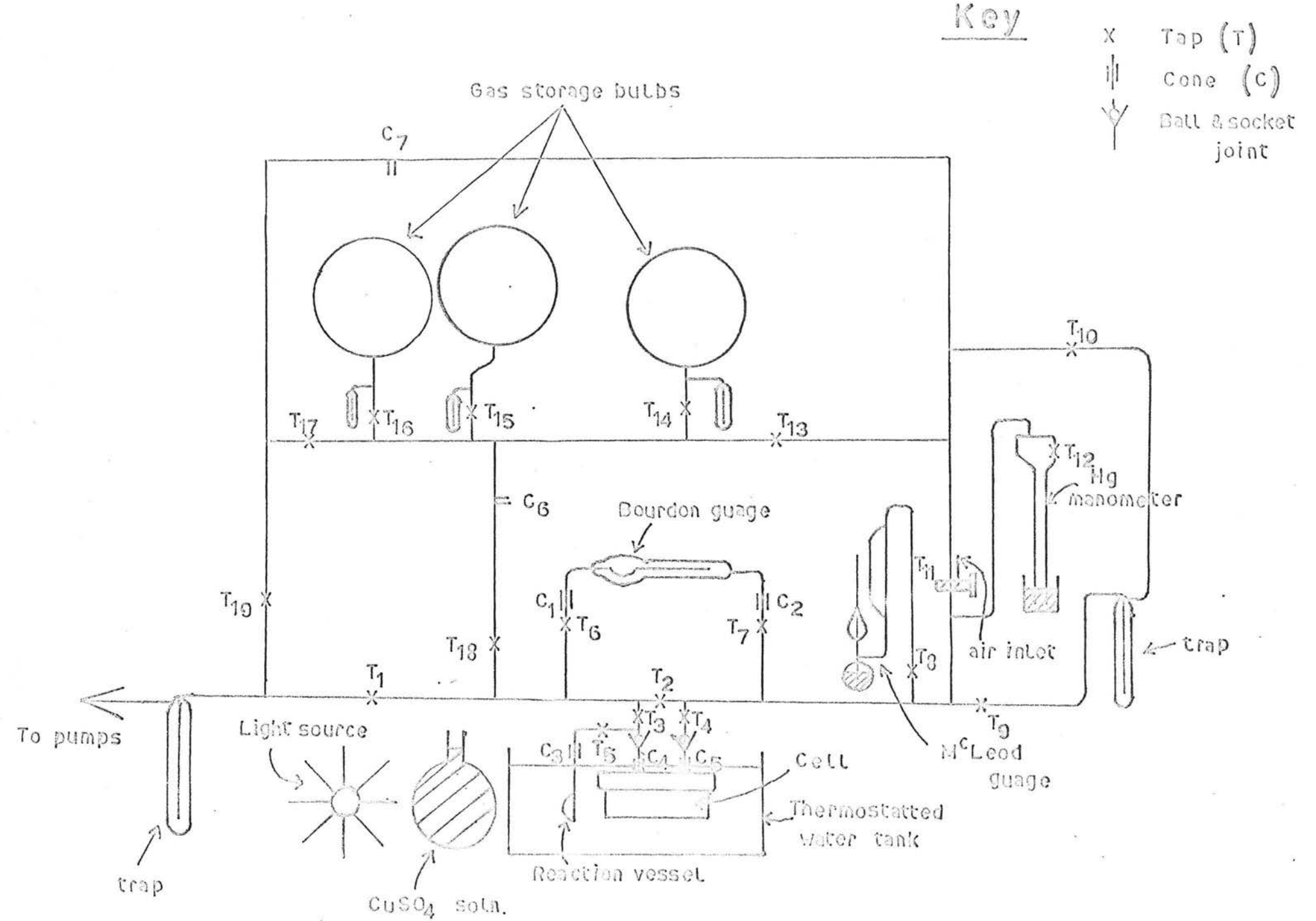

Key
Tap (T)
Cone (C)
Ball & socket joint
Gas storage bulbs
C7
T17
T16
T15
T14
T13
T10
T12
Hg manometer
C6
Bourdon guage
T11
T19
C1
C2
T6
T7
T18
T8
air inlet
trap
T1
T2
T3
T4
T9
To pumps
Light source
C3
T5
C4
C5
Cell
McLeod guage
Thermostatted water tank
trap
CuSO4 soln.
Reaction vessel

Fig 4

EXPERIMENTAL.

A. Apparatus

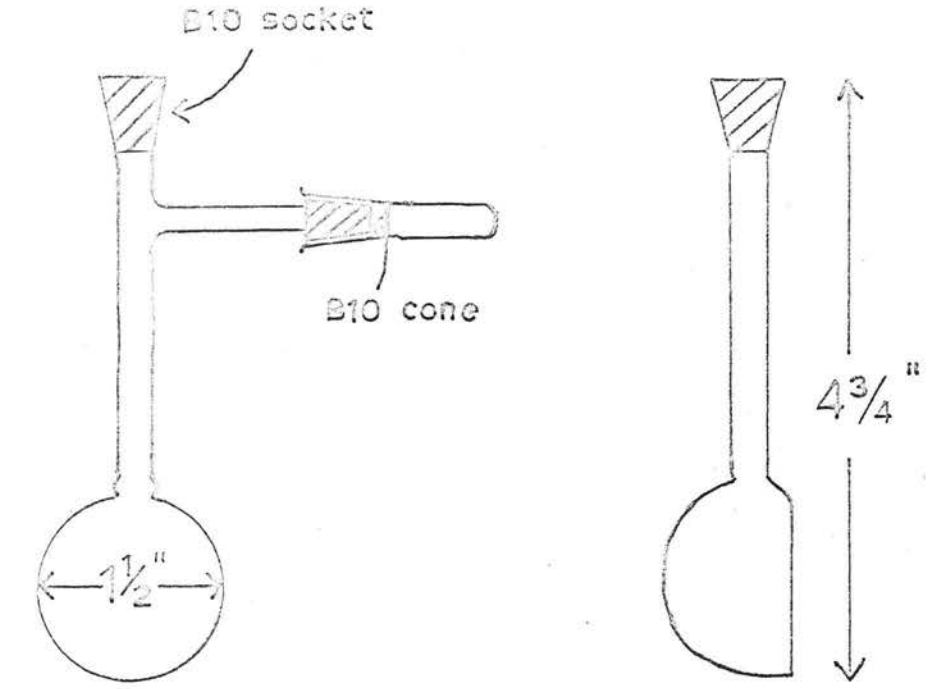
The apparatus was constructed principally from pyrex glass, and consisted essentially of vacuum lines, gas storage bulbs, cold-traps and pressure-measuring devices. (See Fig. 4).

The lines were evacuated by means of a mercury diffusion pump, backed by an oil rotary pump, and pressures down to ca. 10^{-5} mm. Hg were attained. Ground glass joints and vacuum taps were lubricated with Apiezon (L) - high vacuum grease.

TiO_2 films contained in pyrex reaction-vessels of the type illustrated (Fig. 5) were illuminated using a voltage-stabilized mercury-vapour lamp. A Mazda, 250 watt bulb was contained in a protective housing, and the light passed through a flask containing $CuSO_4$ solution (100 g $CuSO_4$ $5H_2O$/litre aqueous soln.) which acted both as a heat-filter and as a focusing lens. The reaction vessels were immersed in a glass-sided water tank, thermostatted at $27 \pm .02°C.$, the water being circulated by a Stuart-Turner pump, and a constant temperature being maintained by an electric heater in series with a contact thermometer and vertical relay unit (Jumo Type G.K.T. 15 - 0.)

Reaction Vessels

In early experiments, discontinuities observed in the 'uptake curves' (See Sec. C(iii)) were considered to be due to water desorbed from the



Reaction vessel

Fig 5

TiO_2 films. For this reason, the reaction-vessels used carried a side-arm which could be charged with P_2O_5, or Na. OH (Fig. 5). Later, however, it became apparent that the presence of such an absorbent had no effect on the uptake, and consequently this practice was abandoned. Subsequently, therefore, the same type of reaction vessel was used, leaving the side-arm empty.

Pressure-measuring devices.

When the pressures were high enough, they were measured on a mercury manometer enabling readings to be made to the nearest 0.2 mm. Very low pressures ($<$ ca. 10^{-2} mm) could be read from a previously calibrated McLeod gauge, and vacua could thus be measured down to $\sim$ 10^{-5} mm.

Generally, however, in the course of following gas-uptakes, it was necessary to measure accurately small pressure changes ($\sim$ 2 mms) at total pressures $\sim$ 30-50 mm. Two devices were available for this purpose.....(1) a Bourdon gauge, and (2) a specially made differential pressure-measurement cell.

(1) The Bourdon gauge was made of soda-glass, and was unthermostatted.

The pointer attached to the spoon was tipped with a small length of Pt wire, and its movement, resulting from a pressure change, could be followed by means of a telescope fitted with a graduated eye-piece. In this way it was possible to measure a total pressure change of ca. 4 mms to an accuracy of $\pm$ 0.01 mm.

Pressure-measurement Cell (actual size)

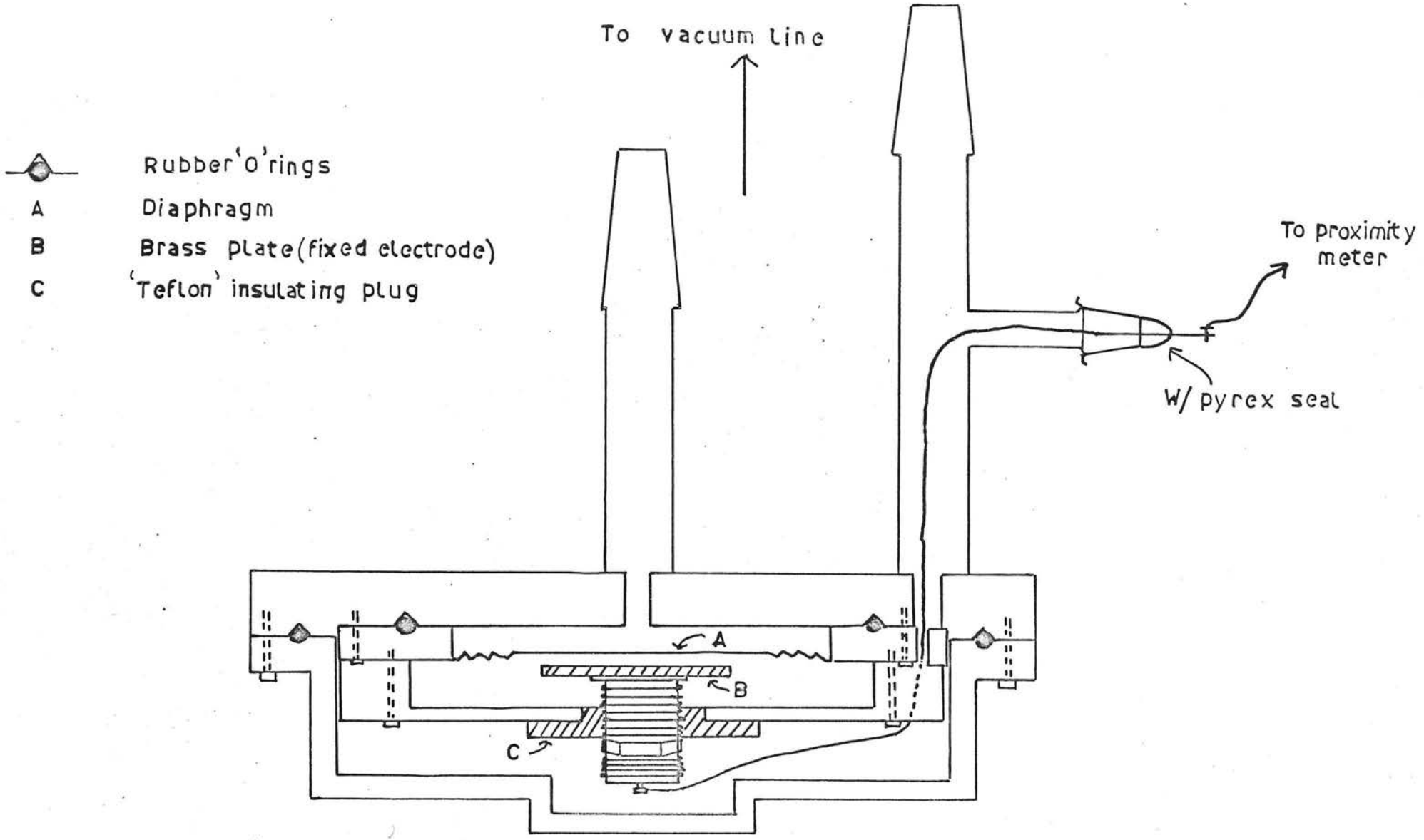


Fig 6

The gauge was calibrated with dry air against the manometer, in the usual way (See, e.g. Ref. (2)). The equilibrium position of the pointer, and the gauge-sensitivity, were not found to alter significantly either with the nature or with the pressure of the gas used.

(2) The Cell was used principally to follow pressure-changes accompanying ad- or de- sorption, and was immersed in the thermostatted water-tank adjacent to the reaction vessel (See fig. 4).

The cell was brass-bound, and was divided into two compartments, separated by a thin corrugated metal-alloy diaphragm (See Fig. 6). Internal, and external, sealing was accomplished using rubber O-rings, so that the whole was vacuum-tight and no leakage took place round the diaphragm. The effect of a pressure-change on one side of the diaphragm was to change its spacing from a fixed (but adjustable) brass plate. The resulting capacitance change was measured on a Proximity meter (Fielden, PM4A), with attached bridge control unit, whose output was fed through a 10 m. v. recorder (Kent Mk 3). This system thus gave, when calibrated, a continuous trace of pressure-change against time.

A more detailed description of the use, and calibration of the cell, will be postponed until Sec. C.

B. Chemicals

(1) Oxygen and Ethylene were obtained from B. O. C. cylinders, and were purified by repeated low-temperature distillation.

(2) Propylene was prepared by dehydration of isopropanol with P_2O_5

$$CH_3\,CH(OH)\,CH_3 \xrightarrow{-H_2O} CH_3\,CH = CH_2$$

The alcohol was added gradually to the P_2O_5 until the reaction had subsided, the mixture was refluxed, and the resulting C_3H_6 passed through a water-cooled condenser, and trapped out at liquid N_2 temperature. The gas was then purified by fractional distillation.

A sample of the gas prepared in this manner was subjected to chromatographic analysis, and no CO_2, O_2 or N_2 was found to be present.

(3) Ammonia was prepared from NH_4Cl and $Ca(OH)_2$, by heating the solid mixture in vacuo.

$$2\,NH_4Cl + Ca(OH)_2 \longrightarrow 2\,NH_3 + 2\,H_2O + CaCl_2$$

The NH_3 was then freed of H_2O by distillation.

(4) Nitric oxide was obtained from the action of nitric acid (1 vol : 1 vol. H_2O) on copper filings in vacuo.

$$3\,Cu + 8\,HNO_3 \longrightarrow 3\,Cu(NO_3)_2 + 2\,NO + 4\,H_2O$$

In addition to the desired product, appreciable amounts of N_2, N_2O and N_2O_4 were obtained, which, however, were easily removed by distillation.

(5) Water vapour was obtained from distilled H_2O which was thoroughly degassed by repeated freezing and pumping.

(6) Titanium Dioxide was prepared by hydrolysis of $TiCl_4$. Two samples were used.....(A) prepared by McLintock (4) and (B) prepared by the author.

Both were prepared in the following manner :-

30 g $TiCl_4$ were added, in small portions, with stirring, to 500 mls. 2.7 M NaCl solution, and the mixture refluxed for 2 hours.

$$TiCl_4 + 2\,H_2O \longrightarrow TiO_2\downarrow + 4\,HCl.$$

The solution was then neutralised with solid NaOH and, after standing, the supernatant liquid was decanted. The TiO_2 was thrown down repeatedly in a centrifuge fitted with a high-speed head, and washed with distilled water until the chloride content was reasonably low. (After several centrifugations, the oxide began to form a colloidal suspension, and became very difficult to throw down. At this point the washing procedure had to be abandoned).

After drying in air at 170°C for 12 hours, and then over P_2O_5 at 100° for 30 hours, the oxide was ground to a fine, white powder and stored in the dark.

TiO_2 prepared in this manner is considered (after Weiser and Milligan (80)) to be largely of the Anatase variety, and has been shown (4, 81) to have surface areas in the order of 100 $m^2 g^{-1}$.

(7) Any other chemicals, e.g. acids, NaCl, CCl_4 etc. were 'Anal R' grade when available. When the presence of impurities was considered to be of possible significance, their nature and influence on the uptakes were examined.

C. Experimental Methods

(i) Calibration of the pressure-measurement cell

The construction of the cell has been described briefly in Sec. A. The effect of setting up a pressure-differential across the metal diaphragm has been stated to cause a corresponding change in capacitance, this being measurable on the proximity meter, or recorder. (The readings on the meter, and recorder, did not coincide exactly, and the practice was made of taking all readings from the recorder chart). The sensitivity of this process could be altered in two ways (a) by adjusting the spacing between the fixed electrode (brassplate) and the diaphragm, and (b) by use of the sensitivity controls on the meter.

In order to demonstrate the way in which the final sensitivity was established, a description will be made of the methods used, from the moment of inserting a new diaphragm, to the final, fine calibration on the vacuum line:-

The diaphragm spacing was first adjusted roughly by means of a butyl phthalate monometer, until a pressure difference of 3 cms ($\equiv$ 3 mms. Hg) was approximately equivalent to a full-scale deflection (100 divisions) on the recorder-chart. The meter sensitivity at this point was normally set arbitrarily at app. $\frac{1}{2}$ x total possible sensitivity.

The cell was then assembled, transferred to the vacuum line (through cones C_4 and C_5) and thoroughly evacuated. Tap T_2 was then closed, thus separating the two halves of both cell and Bourdon Gauge, and dry air

previously stored between T_9 and T_{10} was admitted gradually through T_9. Bourdon gauge and recorder-readings were taken at small pressure-change (Δp) intervals, until it became established whether the cell-sensitivity was higher, or lower than that required ($\sim 0.02^{mm}$Hg/chart division). If necessary, the cell was then removed from the line, the diaphragm spacing altered suitably, and the above procedure repeated. More often, however, the necessary adjustments could be made on the meter sensitivity controls (rough settings 1-12; fine settings 0 - 30).

In this way, the desired sensitivity was attained, and a fine calibration could be carried out.

This was done in the same way as before, by admitting air, O_2, or some other gas to the "non-reaction-vessel side" of the cell, and gauge, in small portions. This simulated conditions obtaining during a gas-uptake, when pressure decreases took place on the "reaction vessel side" of the diaphragm. (The pressure on both sides of the gauge and diaphragm could then be equalised in small steps, by careful use of the connecting-tap T_2).

The above procedure was repeated at different absolute starting pressures, varying from 0 to ca. 5 cms, and at different initial equilibrium recorder-readings. The resulting pressure-changes (in Bourdon gauge divisions, 'ΔB') were then plotted against the corresponding capacitance changes (in Recorder chart divisions, 'ΔR ') and the various diaphragm characteristics noted. These were found to vary from diaphragm to

TYPICAL PLOT OF PROXIMITY METER RESPONSE.
V.S. PRESSURE - CHANGE.

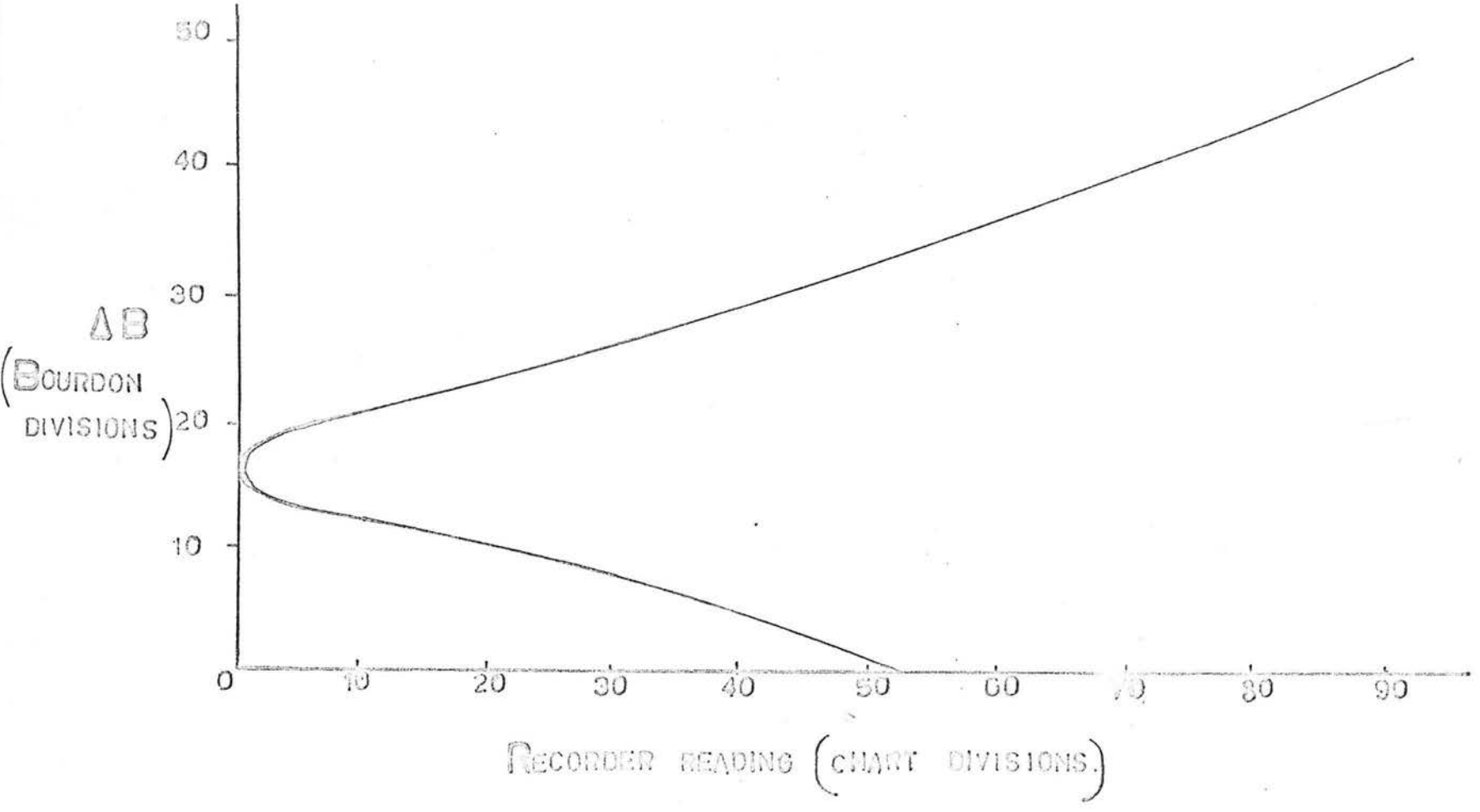


FIG. 7.

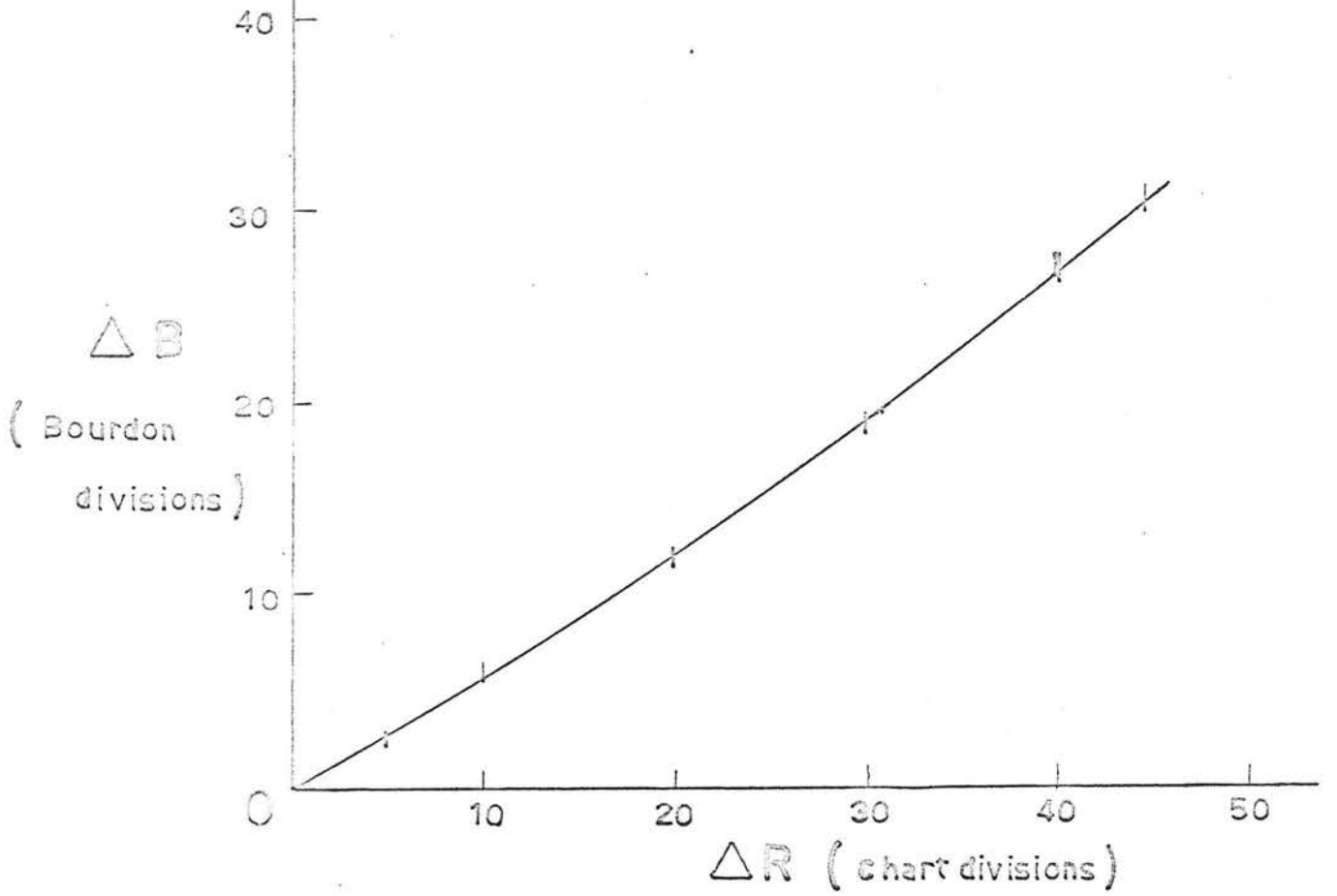

40
30
20
10
0
10
20
30
40
50
Δ B
(Bourdon
divisions)
Δ R (chart divisions)

Fig 8

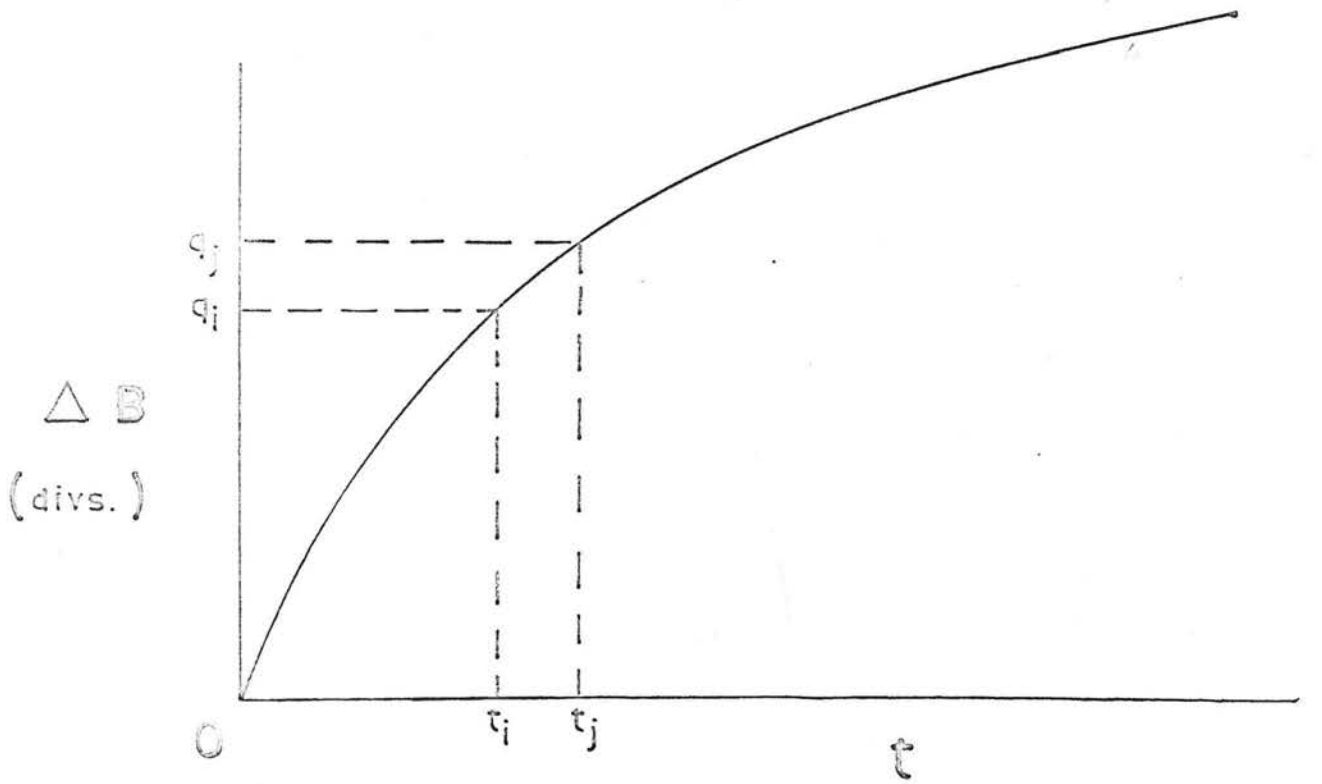

q_j
q_i
0
t_i
t_j
t
Δ B
(divs.)

Fig 9

to diaphragm, but it can be said in general that :-

(1) The sensitivity did not show any significant pressure-dependence, over the range studied, but the zero point (i. e. equilibrium position) of the recorder-pen did change with pressure.

(2) The sensitivity did not alter with different starting positions on the recorder scale, and appeared to be uniform over most of the scale, except near zero when it fell off markedly.

(3) As 'ΔB' increased (equivalent to increasing pressure-decrease on the reaction-vessel side of the diaphragm) the meter reading fell, passed through zero, and then increased up to the maximum scale reading of 100 divs. (See Fig. 7). This was a property of the proximity meter rather than a diaphragm characteristic.

(4) With all the diaphragms used, save one, the sensitivity fell off with increasingΔp (e. g. See Fig. 8). This non-linearity of meter-response necessitated the use, for each diaphragm used, of a calibration plot (ΔB vs. ΔR), so that later values of Δp resulting from gas-uptake could be interpolated from the appropriate ΔR values.

Due to the fall in sensitivity near recorder chart reading 0, adsorption measurements were confined roughly to the scale region 10-90. Since cell sensitivities varied with the diaphragm used, their values will be quoted individually in the appropriate place.

(ii) Preparation of TiO_2 Films

The reaction vessels were first cleaned with a conc. H_2SO_4/H_2O_2 mixture (app. 1:1), washed with water, and thoroughly dried (acetone/compressed air).

Unless otherwise stated, 0.100 g. of finely ground TiO_2 was weighed into the reaction vessel and made into a slurry on the flat face with ca. 0.2 mls. distilled H_2O. The water was then evaporated, with warming and suction at the water pump, taking care to maintain a reasonably uniform thickness of film. It was imperative also to avoid contaminating the optical face of the reaction-vessel with the dioxide, as this would lower the intensity of light incident on the film.

When it was desired to treat the TiO_2 surface with water-soluble solids (e.g. NaCl), the above procedure was repeated using, instead of distilled water, 0.5 mls. of an aqueous solution of the solid of known concentration. After evaporation of the H_2O, most, if not all, of the solid will be left on the surface of the film.

TiO_2 films prepared in the above manner were transferred to the apparatus and pumped in the dark, either in position for reaction (at C_3) at 27°C, or on the upper line (at C_7) at room temperature. The films were never exposed to condensible vapours from the oil pump, these being trapped out with liquid N_2.

Pumping times, and efficiency, varied from case to case .... e.g. sometimes the diffusion pump was used, and sometimes not. There is

reason to suppose that such factors may have great bearing on the subsequent adsorption characteristics, and for this reason data will be given for each individual film in the appropriate place (Experimental Results Sec.) Generally however, films were never given less than ca. 12 hours evacuation with the oil pump only, and never more than ca. 50 hours with the diffusion pump.

Whenever a film was initially evacuated at C_7, its subsequent transfer to the reaction position necessitated its exposure to the atmosphere. The transfer, was however, normally effected in less than 1 minute, and subsequent pumping was for periods never less than ca. $\frac{1}{2}$ hour prior to the experimental run.

After this time no desorption was observable using the pressure-measurement cell, and it was assumed that any atmospheric material (e.g. H_2O vapour) adsorbed during the transfer had been effectively removed.

(iii) Measurement and Kinetic Analysis of Gas Uptakes

Once a TiO_2 film had been prepared and evacuated in the before-mentioned manner, adsorption measurements were carried out in the following way:-

Tap T_5 was closed, thus isolating the reaction vessel from the rest of the apparatus, and the whole system was then isolated from the pumps by closing T_1, and, if necessary, T_{19}. The gas under investigation was admitted from the appropriate storage bulb, through T_{18}, to the Bourdon gauge and cell, to the required pressure as indicated on the mercury-manometer. This pressure was normally in the region 30-50 mm Hg.

It was found at this point that several of the gases studied (e. g. NH_3, H_2O) adsorbed to a lesser or greater extent within the cell itself. This adsorption sometimes took place equally readily on both sides of the cell (and therefore presumably on the brass sides), and sometimes more markedly on the 'non-reaction' side (and therefore probably on the 'Teflon' insulating plug.) In any event, the pressure-decreases accompanying such adsorptions would obviously introduce serious errors into any measurements, made at this juncture, of pressure decreases due to the TiO_2 film itself. Accordingly, in such cases, the gas was allowed to stand in contact with the cell until equilibrium was established, before proceeding with the experimental run. This length of time varied from ca. $\frac{1}{2}$ hour (in the case of C_3H_6) to ca. 5 hours (in the case of NH_3).

After this time, the recorder pen was adjusted to a convenient part of the scale by means of the bridge control, and the chart motor switched on. T_5 was opened, allowing the gas into contact with the film; 10 secs. were

allowed to elapse in order that thermal equilibrium might be established, and T_3 and T_4 were closed, taking a careful note of both the time and the recorder-reading at that point. Any dark pressure decreases were noted, with respect to time, in units of chart-divisions, and the system left undisturbed until a constant reading was obtained over ca. 15 mins. At this point the dark uptake, if any, was deemed to have virtually ceased.

The pressures on each side of the diaphragm were then equalised by opening T_3 and T_4, and the recorder pen, if necessary, readjusted to the original mark. After allowing sufficient time for the Hg vapour lamp to warm up and reach maximum intensity ($\sim$20 mins), the cell and reaction vessel were re-isolated and the light allowed to fall onto the film, noting the precise time and recorder-reading at the moment of commencement of illumination.

The photo-uptake was followed by taking readings initially at half-minute intervals, and then at time-intervals determined by the rate of uptake. In cases where the rate of uptake was so great that the recorder-pen was in danger of passing off the scale, T_3 and T_4 were momentarily opened and re-closed, thus bringing the pen back approximately to the same equilibrium position as before. The change in absolute pressure resulting from this procedure was too small to influence the subsequent rate of uptake, and complete continuity could be preserved, provided that the taps were opened and closed as rapidly as possible.

In this way, a set of 'ΔR' vs. 't' values were obtained,

where ΔR_t = (recorder-chart reading at time 't') - (chart reading at time O), in chart divs.

and t = time from commencement of illumination, in mins.

Pressure decreases, or 'Δp' values were then found, in Bourdon scale divs., from the corresponding ΔR values by interpolating in the appropriate calibration curve, as described in (i).

In order to analyse the kinetics of an adsorption process, the derived Δ p values were plotted against 't' to give the "uptake curve" for that particular photosorption. This curve was obtained by drawing the best possible continuous line through the experimental points, and its typical form is illustrated in Fig. 9.

To derive the rate of uptake at various stages of the uptake, the curve was segmented into suitable (not necessarily equal) small time-intervals, and the mean rate over each interval taken as representative of that corresponsing to the mean uptake over the same interval.

i.e. In Fig. 9, over the interval between t_i and t_j

$$\text{Rate} = \frac{q_j - q_i}{t_j - t_i} \text{ divs min}^{-1}$$

$$\text{and, } \bar{q} = q_i + \frac{q_j - q_i}{2} = \tfrac{1}{2}(q_i + q_j) \text{ divs.}$$

As has been stated earlier (Introduction) the kinetics of photoadsorption have been dominated by two expressions - a "parabolic" expression, and an

exponential, Elovich - type expression. In order to ascertain whether the experimental data fitted either or both of these, suitable linear plots had to be found.

(a) The Parabolic Equation $(q + q_o)^2 = kt + q_o^2$ (k, q_o const; q_o small)

Differentiating, $2(q + q_o)\, dq = k\, dt$

and $dt/dq = \frac{2}{k}(q + q_o)$

Thus, if the parabolic equation is obeyed, a plot of $(\text{Rate})^{-1}$ vs. $\bar{q}$ should be linear with gradient $2/k$ and intercept $2q_o/k$. This plot, therefore, enabled values of k and the small constant q_o to be found. The latter value could then be used to plot $(q + q_o)^2$ vs. t, which should, on the basis of the original equation, be linear with gradient k.

(b) The Elovich Equation $dq/dt = a.e.^{-bq}$ (a, b const.)

Taking logs, $\ln_e dq/dt = \ln_e a - bq$

or, $2.303 \log_{10} dq/dt = 2.303 \log_{10} a - bq$

Thus, adherence to the Elovich equation could be demonstrated by plotting $\log_{10}$ (Rate) vs. $\bar{q}$, which should be linear with gradient $(-b/2.303)$ and intercept $\log_{10} a$.

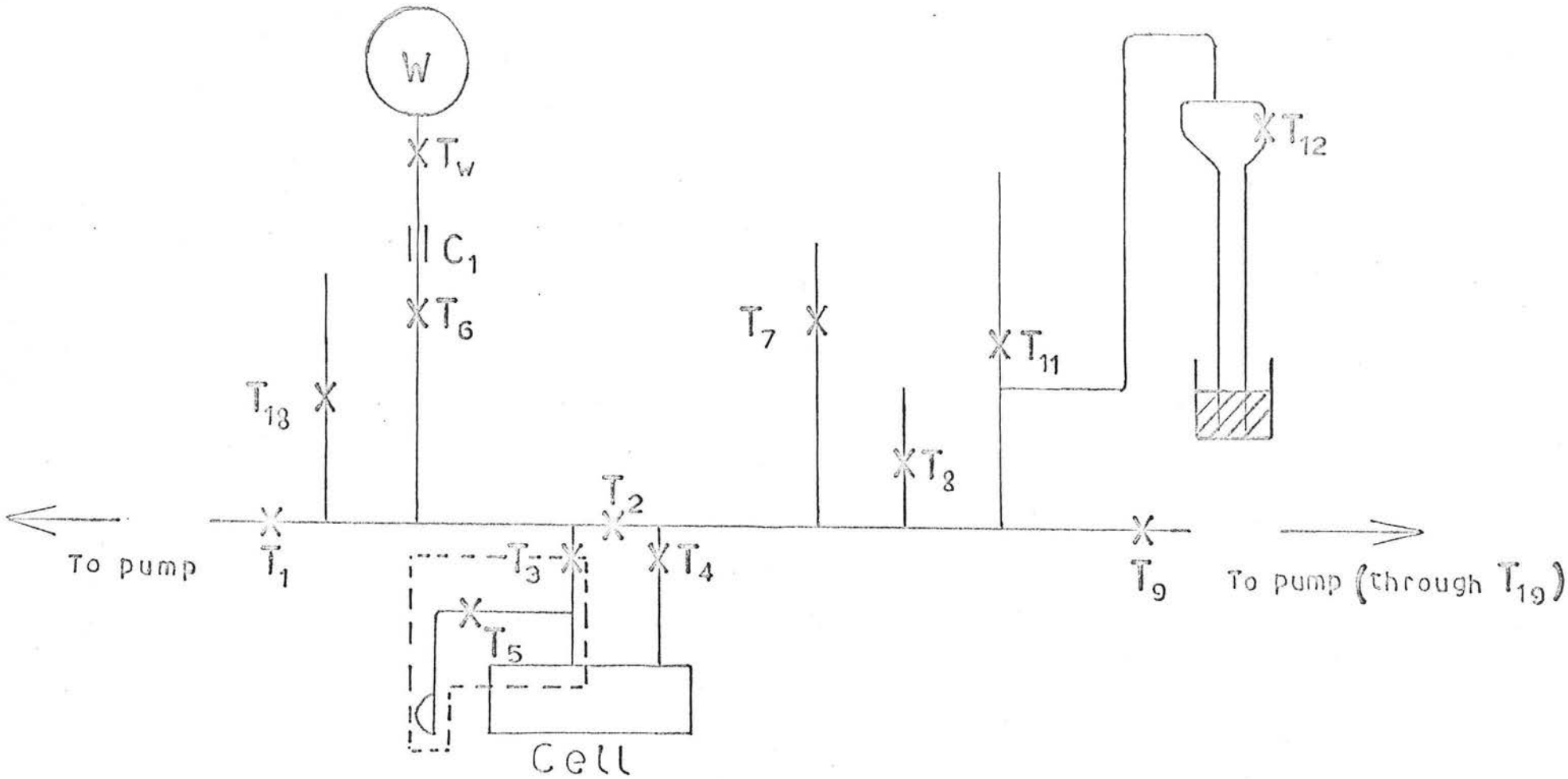

W
T_w
C_1
T_6
T_{13}
T_7
T_{11}
T_{12}
T_8
T_2
To pump
T_1
T_3
T_4
T_5
T_9
To pump (through T_{19})
Cell

Fig 10

(IV) Determination of the Reaction Space Volume

By the term 'reaction-space' is meant that volume within which pressure-changes were measured during an uptake, as in Sec.(iii). Knowledge of this volume was obviously required before these pressure-changes could be expressed in molar terms.

Normally, uptakes were measured within the space including the reaction vessel, the leads to the cell below T_3, and that volume within the cell to the "reaction side" of the diaphragm..... i.e. that part of the apparatus enclosed by the dotted line, in Fig. 10.

In principle, the reaction-volume may easily be determined by expanding a known pressure of air from the latter into a bulb of known volume, and reading the new pressure.

In practice, however, this procedure was complicated by the requirement that only very small pressure-differentials could be applied across the diaphragm, and Bourdon gauge, without damage to these. It was found necessary to remove the Bourdon gauge from the apparatus, and to insert the bulb of known volume, W, on C_1. The section of the modified apparatus involved is shown in Fig. 10.

Procedure :-

That part of the apparatus between T_1, 18, 7, 8, 11 and 9 was evacuated and isolated. About 30 cms. of dry air were introduced, through the air inlet attached to T_{11}, to the whole of this section, and the pressure read

carefully on the manometer..... P_1

T_2 and T_3 were closed, and T_1 opened to the pump. After evacuation, T_1 and T_w were closed. T_3 was then opened fractionally (to give a meter-response ~ 50 divs), reclosed, and the recorder brought back approximately to the equilibrium position by very careful pumping through T_9. This procedure was repeated until there was no change in the recorder-reading on opening T_3. At this point, therefore, the pressures on both sides of T_2 were very nearly equal. Again, a careful manometer-reading was taken..... P_2

T_w was now opened fractionally, with alternate pumping through T_9 as before, until there was no change on the recorder. The air was thus at this point completely expanded from the reaction-volume, V, into W, at a final pressure read from the manometer, of..... P_3

Let the volume of the reaction-space be 'V' mls

" " " contained between T1, T_{18}, T_w, T_2 be 'X' mls

" " " of the bulb be 'W' mls

Then, assuming ideal-gas behaviour,

$$P_1V = P_2(V + X) = P_3 (V + X + W)$$

From these equations, it can be easily be shown that

$$V = \frac{P_2P_3}{P_1(P_2-P_3)} \quad W \text{ mls}$$

so that, if W is known, V may be found from P_1, P_2 and P_3.

Since it was seldom required to determine molar quantities, and then only approximately, the above determination was carried out for only one of the three reaction-vessels used, which did not differ appreciably in size.

Results

Volume of bulb (W) = 48.2 mls.

Two determinations were made, excellent concordancy of results being obtained:-

	P_1	P_2	P_3	(cm. Hg)	$V = \frac{P_2 P_3}{P_1(P_2 - P_3)}$ W (mls)
A.	29.10	14.90	10.47		58.2
B.	34.10	17.37	12.25		58.6

V was thus taken to be approx. 58 mls.

(V) Analysis of Reaction Products

Following a photo-uptake, or reaction, unused reactants and products (if any) were either in the gas phase, or were sorbed to the TiO_2 and, possibly, to the cell interior.

When an analysis of the resulting system was desired, the normal procedure was first to allow the vapours to stand in contact with a trap surrounded by liquid N_2 (Temp. 77°K). Any gas not condensed at this temperature was generally assumed to be O_2 unless the circumstances suggested the possible presence of some other permanent gas (e.g. N_2, H_2, CO). Once any pressure changes accompanying this procedure had gone to completion, the remaining vapours in contact with the film were pumped slowly through the cold-trap (by opening T_{10} and T_{19}). In this way, non-condensible gases were removed from the apparatus, and condensible material sufficiently weakly bound to the TiO_2 surface (and possibly to the cell interior) was transferred to the trap. The amount of reactants and products present in the trap could easily be found at any time by isolating from the pumps, removing the liquid N_2, and allowing the gases to expand into the pressure-measurement system. The pumping procedure was continued for lengths of time depending on the nature of the gases to be examined..... eg CO_2 was found to be bound relatively weakly to the TiO_2, and was usually completely removed by ca. 1 hour's pumping, whereas H_2O was much more slowly desorbed. Generally, however, the pumping was continued through the cold-trap overnight, the

TiO_2 film being maintained at the thermostat temperature of 27°C.

The condensible reactants and products obtained in this way were then analysed qualitatively and quantitatively by one or both of two methods - (a) by vapour-pressure analysis, and (b) by gas chromatography.

(a) Vapour-pressure Analysis

When the vapour-pressure vs. temperature curves of the various components of the analysis-mixture were well separated, the components themselves could be separated, identified and estimated by this means.

Temperatures were measured either with a low-temperature thermometer, or by means of a calibrated thermocouple. In the latter case, one junction of the thermocouple was taped to the foot of the cold trap containing the mixture, and the other was immersed in ice and maintained at 0°C. The temperature of the cold-trap was raised by substituting, round the trap, a thermos flask chilled to liquid N_2 temperature for that containing the liquid N_2, and allowing the temperature to rise slowly and spontaneously, taking readings of thermo-current when necessary. If required, the rate of temperature-rise could be increased by occasional blowing of air at room-temperature into the Thermos, and allowing sufficient time for equilibrium to be established before each reading.

Pressures corresponding to the temperature-readings were measured on either the manometer or the Bourdon gauge, according to their magnitude. Use of the cell for this purpose was avoided, owing to the possibility of

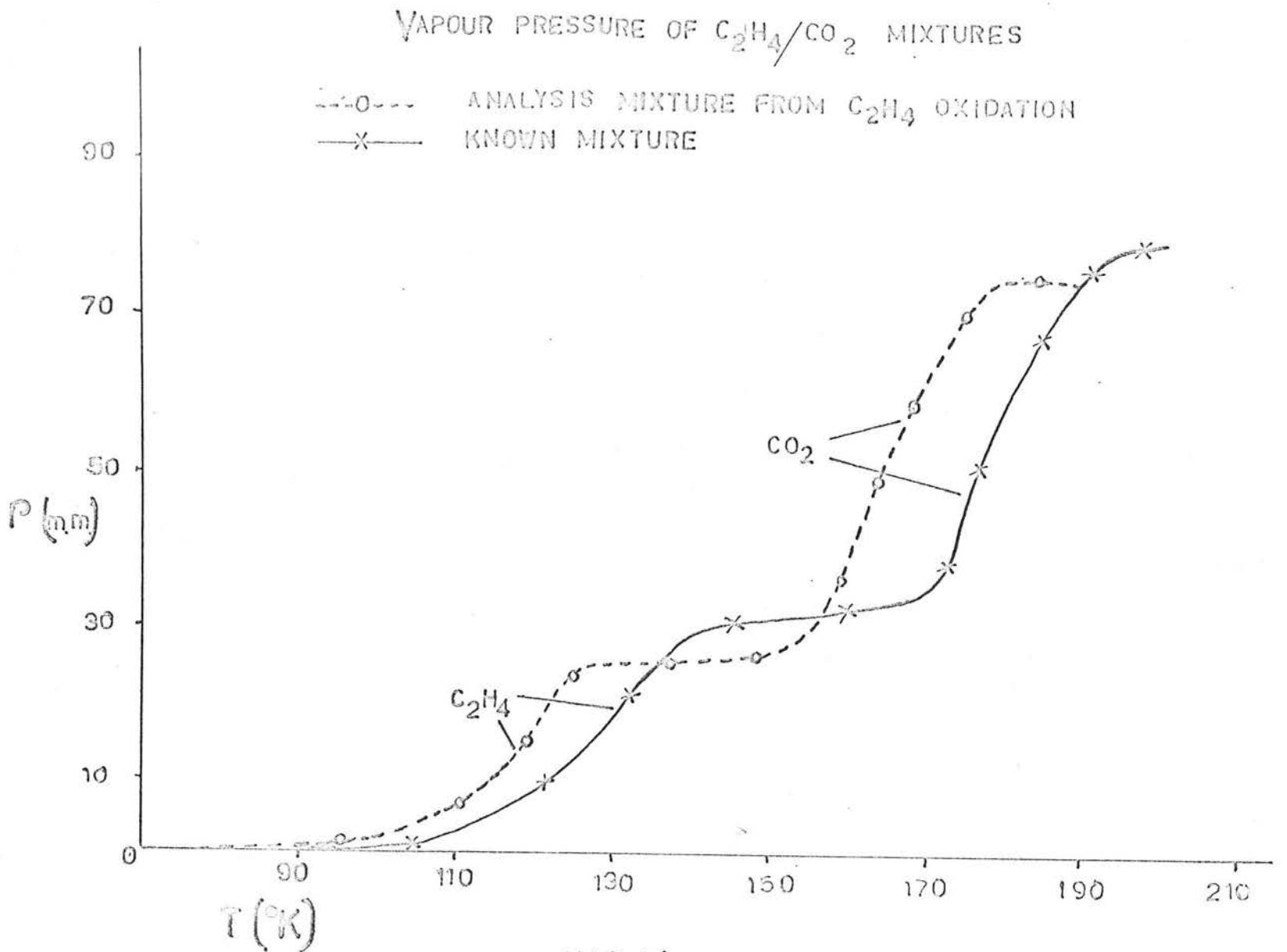

VAPOUR PRESSURE OF C_2H_4/CO_2 MIXTURES
ANALYSIS MIXTURE FROM C_2H_4 OXIDATION
KNOWN MIXTURE
90
70
50
30
10
0
P (m.m)
CO_2
C_2H_4
90
110
130
150
170
190
210
T (°K)

FIG. 11.

Vapour pressure of a C_3H_6/CO_2 mixture.

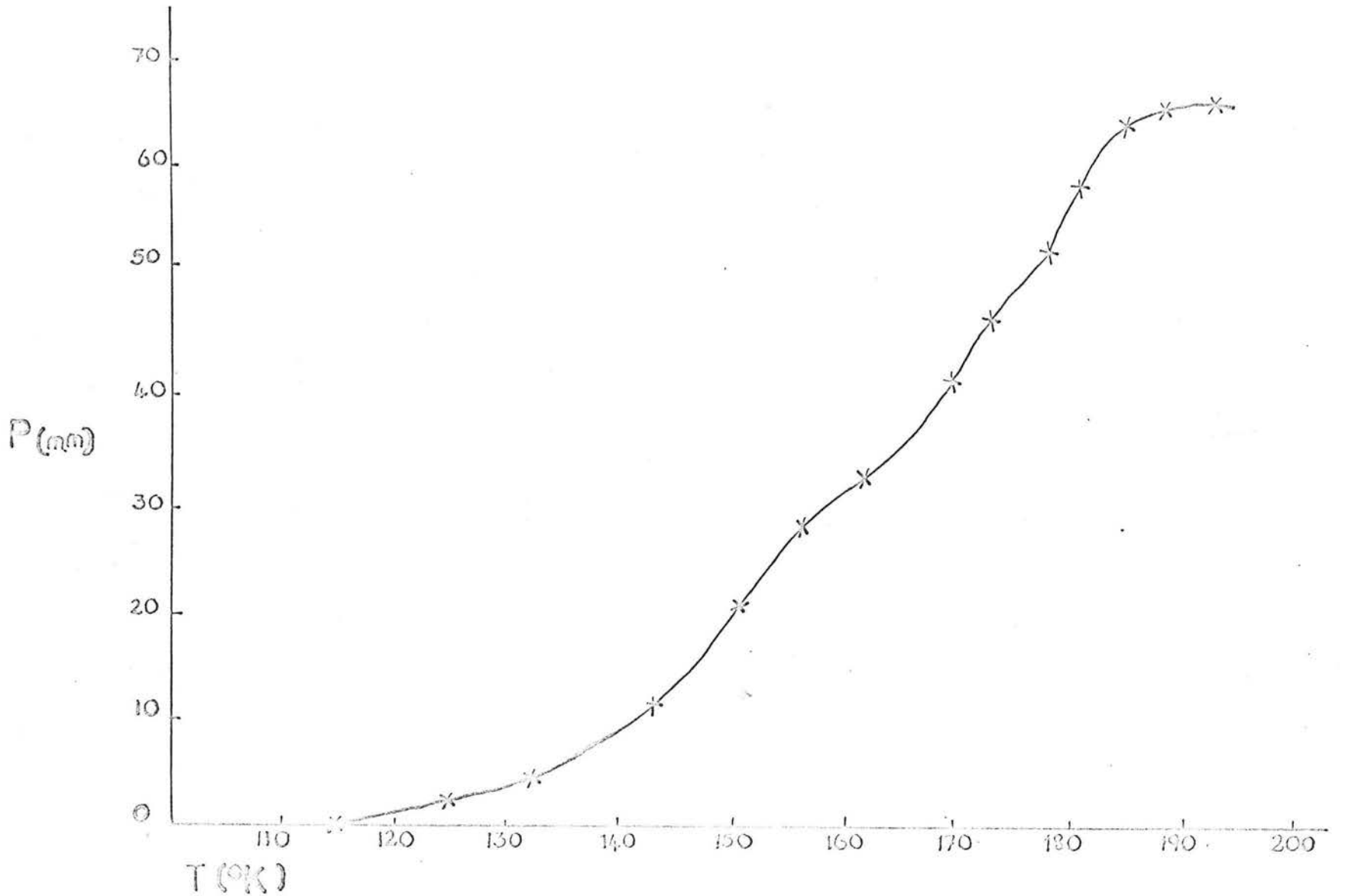


FIG. 12.

adsorption on the brass. The volumes in which these pressure-measurements were made varied from time to time. The tap to the reaction-vessel, T_5, was always kept closed in order to avoid readsorption on the TiO_2, and when the same was likely to occur in the cell, it too was isolated. It was easy to correlate these measurements with starting-pressures within the reaction volume, by observation of the pressure-changes resulting from expansion of dry air from one volume to the other.

It was found that reasonably reproducible vapour-pressure curves could be obtained in the above manner, provided that care was taken not to allow the temperature of the trap to rise too rapidly. Seldom, however, was good agreement obtained between experimentally determined vapour-pressures and literature values (I. C. T. and Rubber Handbook), except at very low pressures ($\sim$ 1-10 mms.). It was always necessary, therefore, to compare the experimental curve for an unknown gas with the similarly determined curve of a known gas, before complete identification could be achieved.

As an example of the type of plot obtained, Fig. 11 shows the curve resulting from the analysis mixture of a C_2H_4 oxidation, compared with that of a known C_2H_4/CO_2 mixture.

Some gases, however, had vapour-pressures which were too close together to permit easy separation by the above procedure. It was found, for example, that a C_3H_6/CO_2 mixture gaverise to the curve shown in Fig. 12, where no definite break is discernible. In this case, therefore, the

Gas chromatography of a C_3H_6/CO_2 mixture.

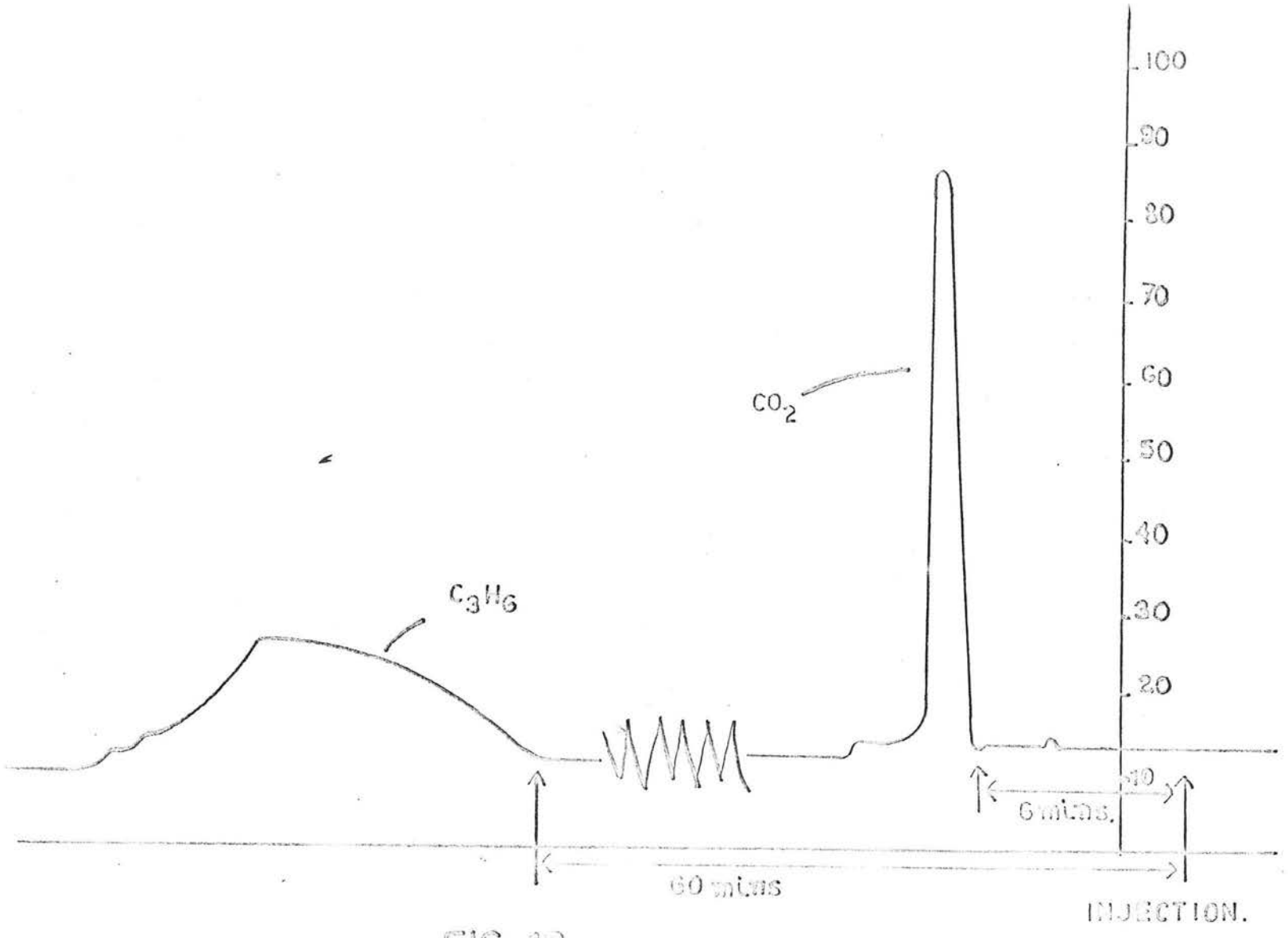


FIG. 13.

second of the two methods was adopted:-

(b) Gas Chromatography

Propylene/carbon dioxide mixtures were passed through a silica-gel column maintained at 35°C, the carrier gas being H_2, and the flow rate normally being adjusted to ca. 20 ml. min^{-1}. Detection was by a catherometer whose resistance-changes were recorded.

It was found that, under these conditions, the retention-time for CO_2 was ca. 6 mins, whereas that for C_3H_6 was ca. 60 mins. - i.e. good separation was obtained. The CO_2 peaks were sharp and symmetric, but C_3H_6 appeared as a broad asymmetric band. An example of the type of chromatograph obtained is shown in Fig. 13. Consequently, for calibration and quantitative estimation purposes, CO_2 was measured from its peak height, and C_3H_6 from its band-area, this area being estimated by planimeter.

Products and unused reactants remaining on the TiO_2 surface following the pumping procedure described earlier, represented, to a large extent, unknown quantities. On some occasions, however, the TiO_2 film was extracted with a suitable solvent - usually water, and the resulting solution examined by normal analytical methods. For example, the TiO_2 surface was examined for the presence of formaldehyde by testing the aqueous extract with chromatropic acid in 72% H_2SO_4 (82).

It must be emphasised, however, that a negative result obtained from a test of this nature did not necessarily preclude the existence of the suspected product on the surface, since the strength of binding might be too great to permit extraction by this means.

Part 3

EXPERIMENTAL RESULTS

EXPERIMENTAL RESULTS

I Uptake of Oxygen, hydrocarbon and oxygen/hydrocarbon mixtures on untreated TiO_2

The adsorptions of O_2, C_2H_4, C_3H_6 and of C_2H_4/O_2 and C_3H_6/O_2 mixtures were followed at 27°C, using the procedure outlined in Experimental Sec. C (iii), on TiO_2 films evacuated in the normal way, and "untreated" in the sense that no other adsorbate was placed on the surface prior to the experimental run.

Since in the course of such experiments, several different diaphragms were used, and meter-sensitivities were varied from time to time, correspondingly differing capacitance vs. pressure-change characteristics were obtained. In order to avoid confusion, therefore, it has been made the practice to indicate derived pressure-changes in units of Bourdon gauge divisions (' Δ p'), in the manner described in Experimental Sec. C, except in those cases where comparative quantitative results were not required, when it was sufficient to quote 'ΔR' values (Recorder-chart divisions). Bourdon gauge sensitivities are quoted where appropriate, as are other variables such as gas-pressures. The weights of TiO_2 used and the reaction-volumes were, unless otherwise stated, 0.100 g. and 58 mls. respectively.

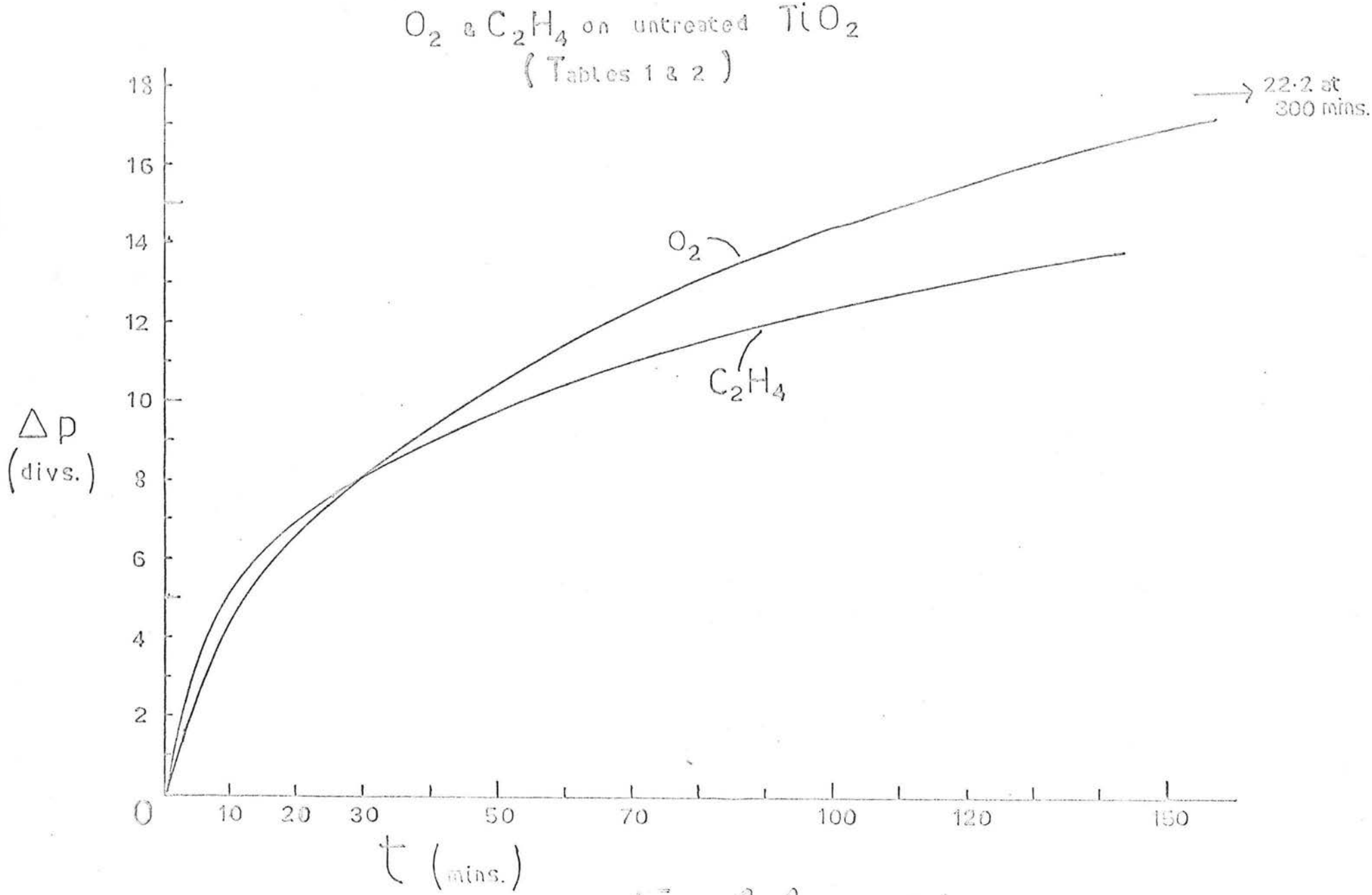

O_2 & C_2H_4 on untreated TiO_2
(Tables 1 & 2)
22·2 at 300 mins.
O_2
C_2H_4
Δp (divs.)
0
2
4
6
8
10
12
14
16
18
10
20
30
50
70
100
120
150
t (mins.)

Fig 14

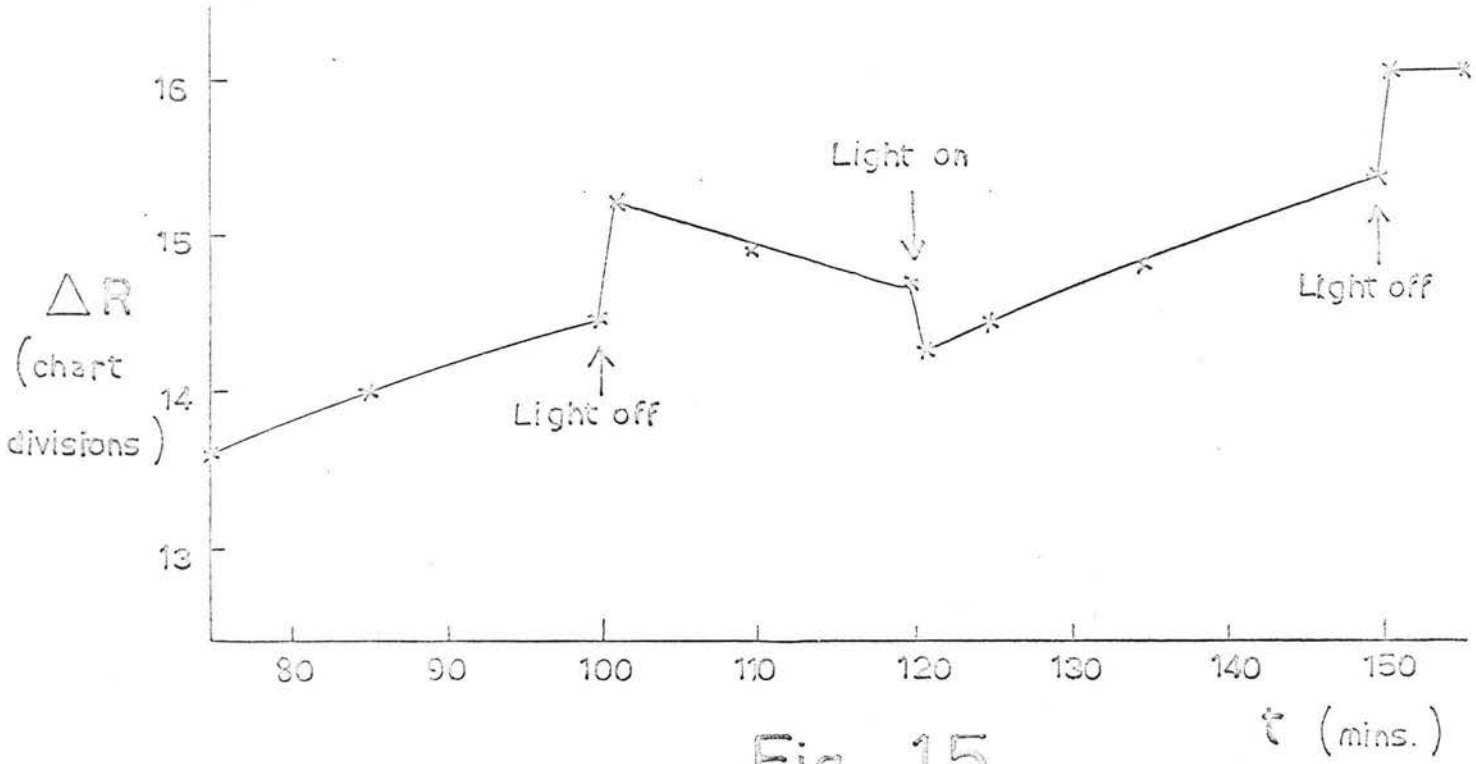

16
15
14
13
ΔR
(chart
divisions)
Light on
Light off
Light off
80
90
100
110
120
130
140
150
t (mins.)

Fig 15

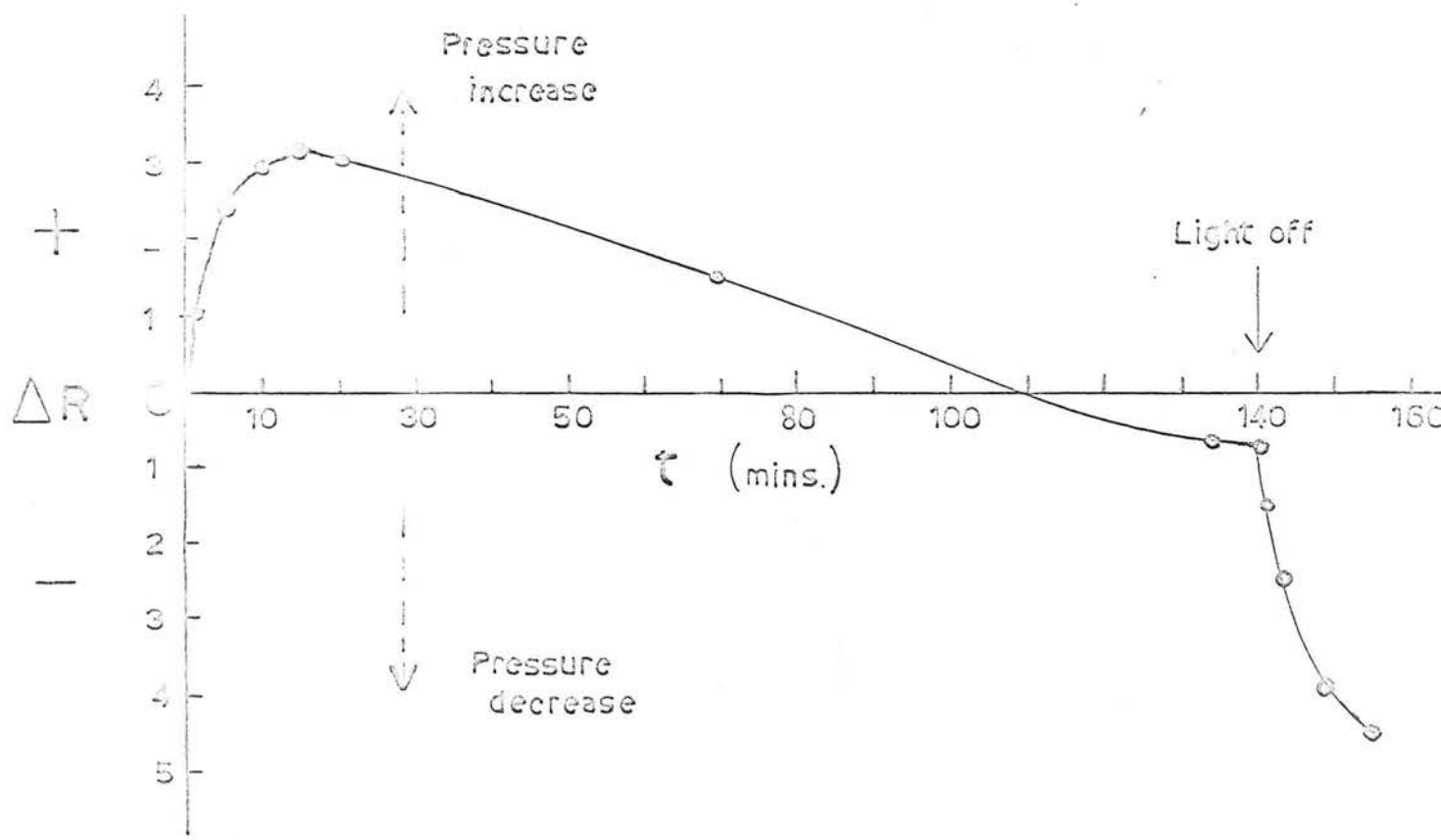

Pressure
increase
4
3
+
1
ΔR
0
1
2
3
4
5
—
10
30
50
80
100
140
160
t (mins.)
Light off
Pressure
decrease

Fig 16

Typical pressure-decrease data for oxygen and ethylene are presented in Tables 1 and 2, and the corresponding 'uptake curves' are illustrated in Fig. 14. It was found in general that O_2 was taken up in greater amounts than was C_2H_4, though often the initial rate of uptake was greater in the case of C_2H_4. A very small dark uptake ($\sim$ 2 chart divs.) was observed with C_2H_4, but not with O_2. This uptake had normally reached conclusion after ca. 15 mins., and has not been included in photo-uptake plots such as Fig. 14. A detailed analysis of the kinetics of these processes will be presented later.

A feature of the C_2H_4 uptakes which quickly became apparent is illustrated in Fig. 15, which shows the effect of ceasing illumination in the later stages of uptake. An immediate pressure decrease (of ca. 1 - 3 chart divisions) always took place, which was reversed on recommencement of illumination. The same effect was later encountered with C_3H_6 and, to a lesser extent, with NH_3, but not with O_2.

It seemed probable that this phenomenon was associated with a heating effect caused by the light-beam (the thermal conductivities of the gases are in the order $C_2H_4 < NH_3 < O_2$), and therefore experiments were devised in order to test this possibility.

In one experiment, a reaction-vessel, immersed in the

Effect of interruption of illumination

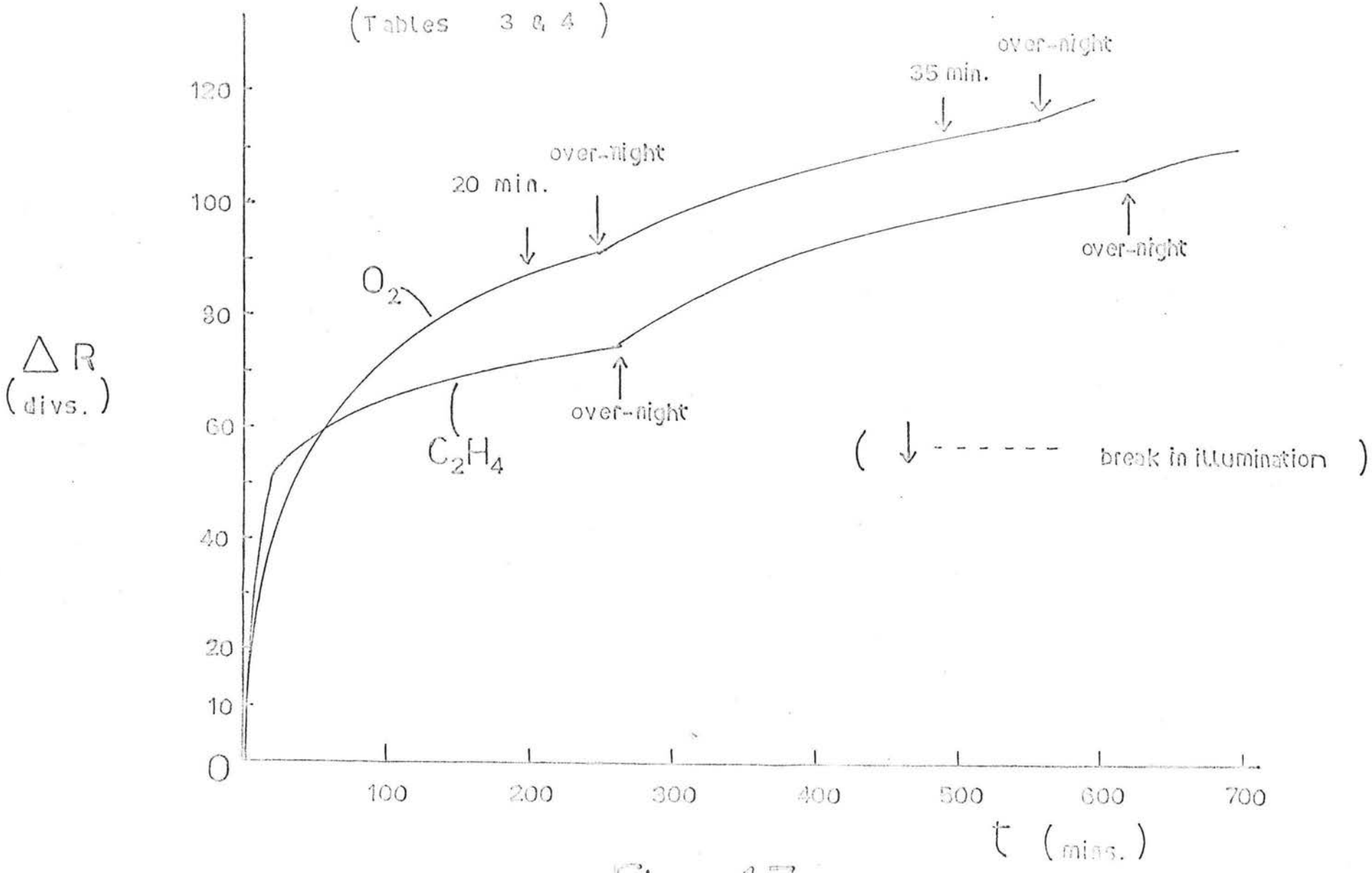


Fig 17

(unthermostatted) water-tank and containing 50 mms. C_2H_4, was illuminated in the absence of TiO_2. Small pressure-changes corresponding with those observed during the uptakes were indeed observed, but these were too small ($\sim$ 0. 3 div.) to permit any conclusive interpretation. It appeared likely that the presence of the strongly reflecting TiO_2 was required before the thermal pressure-changes became appreciable.

The same experiment was carried out, therefore, this time using a reaction-vessel whose outside face was coated with a TiO_2 film, thus simulating, as nearly as possible, the conditions obtaining during an uptake experiment. In this case, however, it was not possible to immerse the vessel in water. The results are shown in Fig. 16, and clearly indicate that the observed sudden pressure changes were indeed due to the heating effect of the light-beam. The fact that no similar changes were observed with O_2 is presumably explained by the relatively high thermal conductivity of this gas (5.63×10^{-5} cal. sec^{-1} cm^{-2}/unit temp. grad. Cf. C_2H_4 3.95×10^{-5}).

A further way in which the C_2H_4 uptakes differed from those of O_2 with respect to interruptions in illumination is exemplified by Fig. 17 (Tables 3 and 4). It was found that if, following a photosorption, the pressures on each side of the diaphragm were

equalised, and the C_2H_4/TiO_2 system allowed to stand in the dark for an appreciable length of time - often overnight - recommencement of illumination gave rise to initial rates of uptake much greater than those immediately prior to cessation of illumination, i. e. discontinuities, or 'steps' became apparent in the uptake curve. The same was found to be true if the gas was removed and the film allowed to stand in vacuo during the dark period, before recommencing the photo-uptake.

Similar effects were observed on occasions during O_2 photo-adsorption, but the discontinuities were here much less pronounced (Fig. 17, Table 4). Other authors (e. g. 2, 77) have attributed these irregularities as being due to desorption of binding liquid - here water - from the film-surface. It seemed logical, therefore, to examine the effect of incorporating a drying agent within the system, on the adsorption characteristics. For this purpose, several adsorptions were examined, charging the side-arms of the reaction vessels with P_2O_5, or with NaOH, the latter having the additional property of being capable of absorbing any CO_2 evolved from the film. It soon became apparent, however, that the presence of such an absorbent did nothing to remove the "overnight steps" from the uptake curves, and, if anything, seemed to accentuate the latter. (An example where the

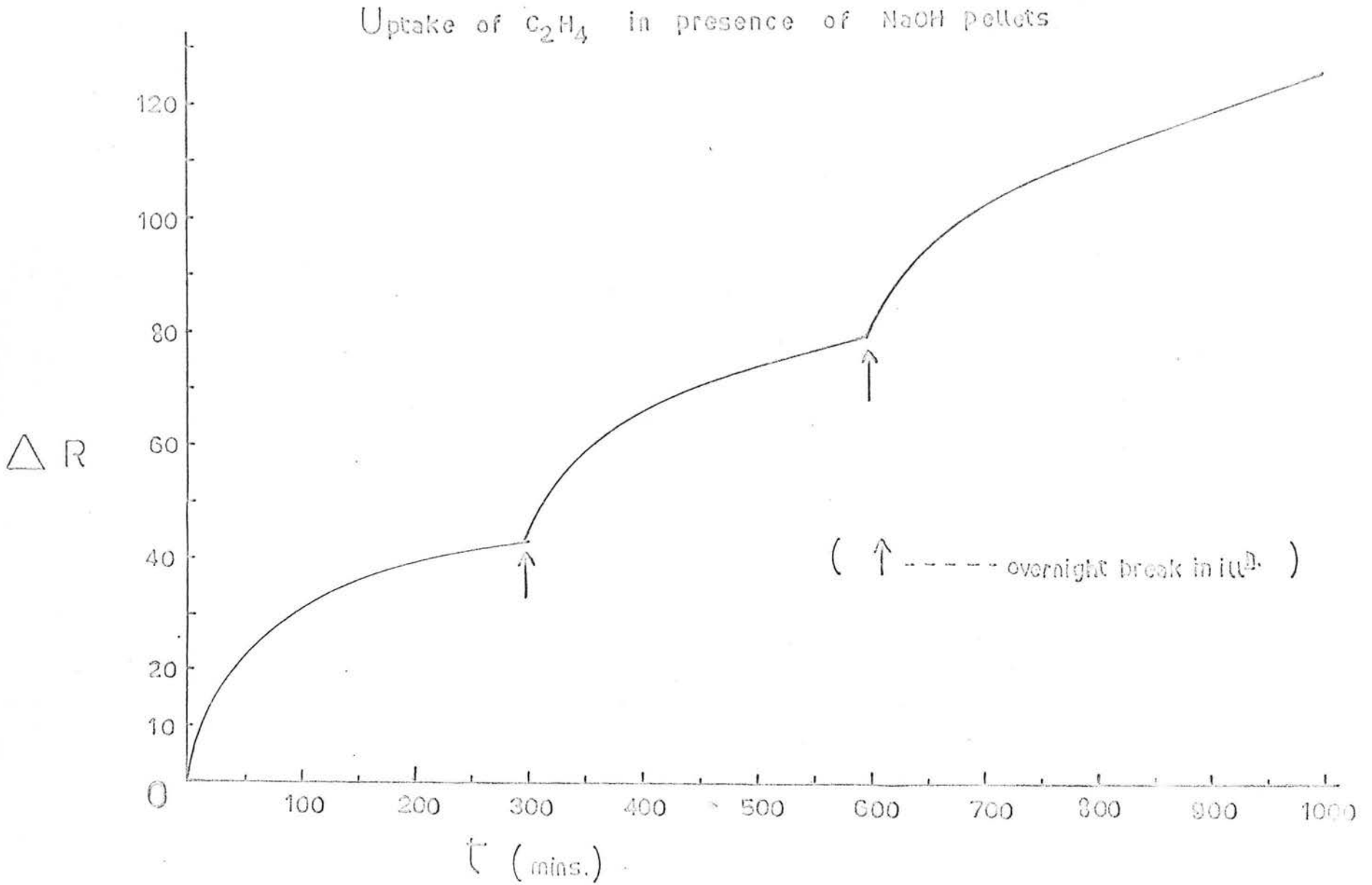

Uptake of C_2H_4 in presence of NaOH pellets
120
100
80
60
40
20
10
0
△ R
100
200
300
400
500
600
700
800
900
1000
t (mins.)
(↑ ----- overnight break in it^n.)

Fig 18

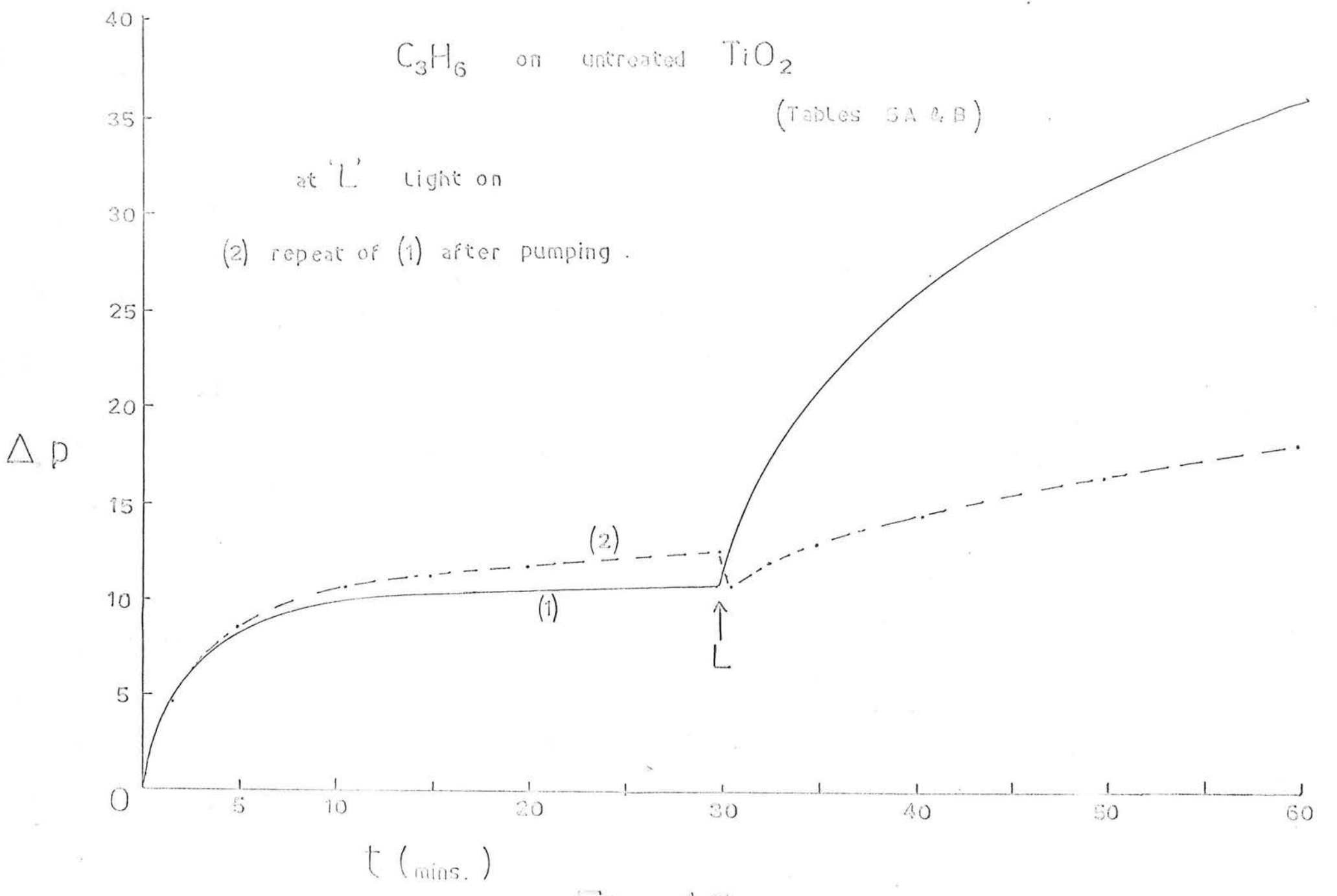

C_3H_6 on untreated TiO_2
(Tables 5A & B)
at 'L' Light on
(2) repeat of (1) after pumping .
Δ p
t (mins.)
(1)
(2)
L
0
5
10
20
30
40
50
60
5
10
15
20
25
30
35
40

Fig 19

discontinuities were particularly pronounced is shown in Fig. 18). In view of these results it seemed unlikely that H_2O (or CO_2) was being desorbed in significant quantities during the course of a typical uptake, and in future experiments, therefore, the absorbent was omitted.

The adsorption of propylene presented a different picture from that of C_2H_4 or O_2 in that a significant dark uptake was observed. The extent of this uptake varied from film to film, but was normally in the region of 10 - 15 chart divisions, and had usually virtually ceased after ca. 40 mins. Illumination then led to further, more extensive pressure - decreases, these being roughly of the same magnitude as the C_2H_4 photo-uptakes. (Fig. 19, Tables 5A and B). The same thermal pressure effects associated with the light beam, were encountered as with C_2H_4, and, again, overnight stands in the dark resulted in increased initial rates of photo-uptake.

The results of Tables 5A and 5B (Fig. 19) show the dark sorption to be reversible, in that a repeat uptake on the same film, following evacuation, followed much the same path as the original uptake, and was, in fact, slightly greater in magnitude. This was not true for the photo-uptake which may, therefore, be concluded to be, at least largely irreversible.

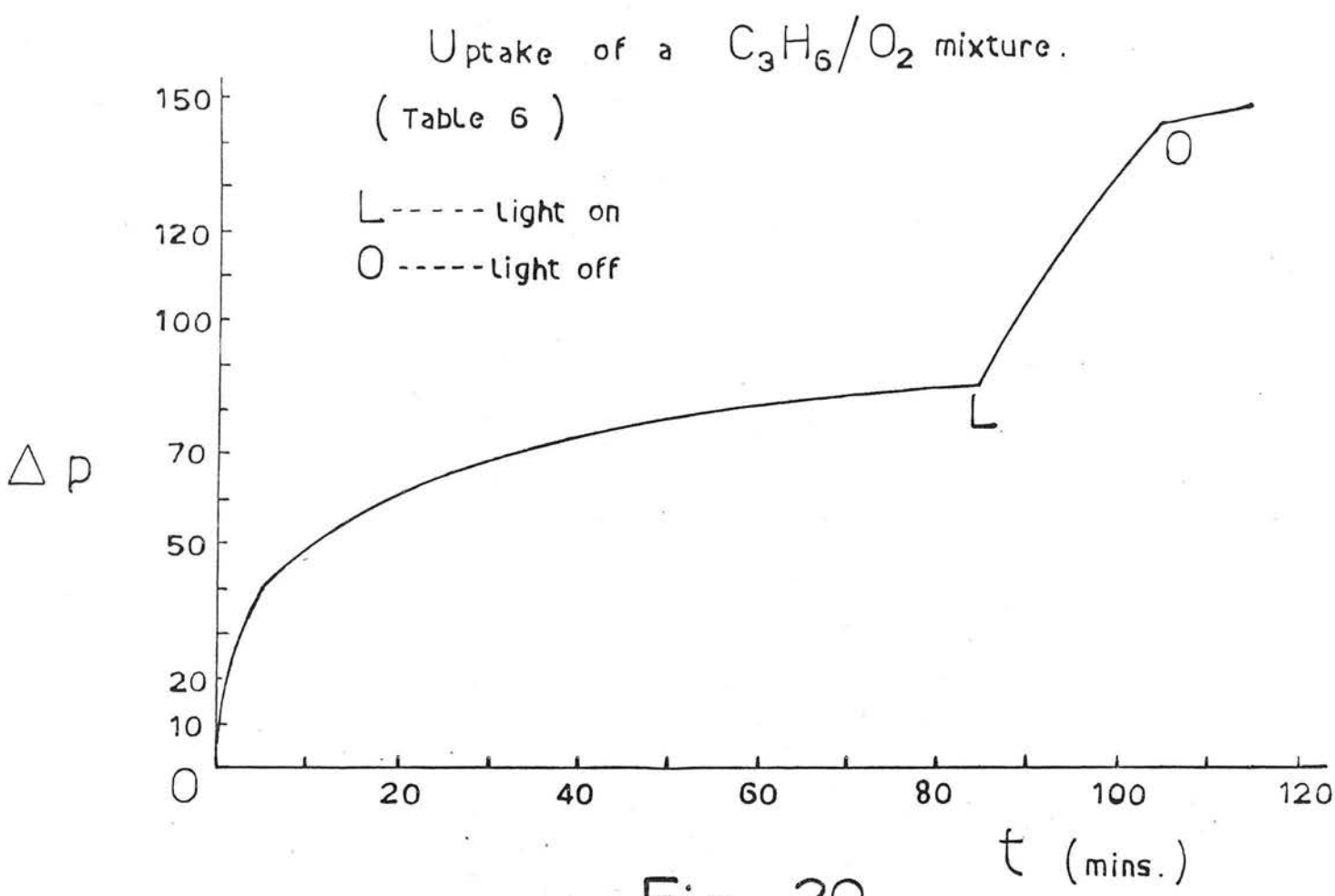

Uptake of a C_3H_6/O_2 mixture.
(Table 6)
L------ Light on
O------ Light off
150
120
100
70
50
20
10
0
Δ p
20
40
60
80
100
120
t (mins.)
L
O

Fig 20

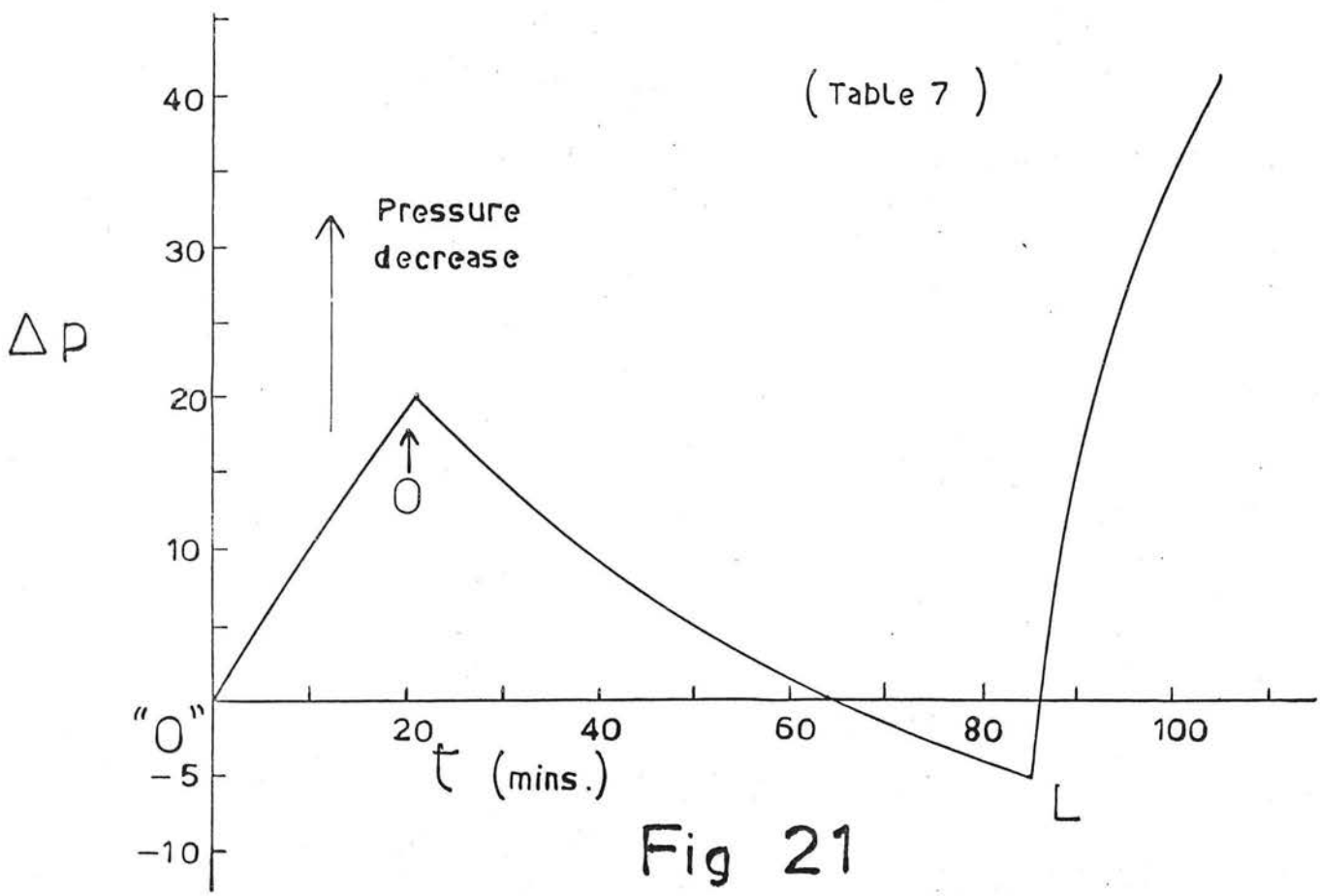

(Table 7)
Pressure decrease
40
30
20
10
"0"
-5
-10
Δ p
20
40
60
80
100
t (mins.)
O
L

Fig 21

The uptakes of hydrocarbon/O_2 mixtures were found to be extremely rapid and extensive. Generally the pressure decreases occurring in such systems were much greater than would be expected for the sum of the two separate uptakes - e. g. in one experiment the pressure-decrease after 60 mins. illumination of an C_2H_4/O_2 mixture was Δp = 73 divs. (sensitivity 0. 050 mm. $div.^{-1}$), this being approximately three times the expected uptake if the adsorptions were taking place independently of one another.

The general form of the uptake curves for the mixtures was the same as for the uptakes of the pure components - i. e. Δp decreased with time. Again, a discussion of the kinetics will be postponed until later.

Only very small dark pressure- decreases were observed with C_2H_4/O_2 mixtures, but considerable dark uptakes of C_3H_6/O_2 mixtures were noted, (Fig. 20, Table 6), these being generally much greater than expected for pure C_3H_6. As with C_3H_6 itself, the dark uptakes were reversible by evacuation, and, once they had gone virtually to completion, the effect of illumination was, again, to cause further rapid and extensive adsorption (Fig. 20, pt. 'L').

A result of interest in this connection is illustrated in Fig. 21 (Table 7). The same film as was used in deriving the data of

Table 6 was illuminated in 42 mm. C_3H_6 : 14 mm. O_2 overnight. The film was then pumped, using the diffusion pump, for 2 hours, and re-illuminated in 36 mm. C_3H_6 : 14 mm. O_2 for 19 hours. After this time, a pressure decrease was still taking place at the rate of approx. 0.5 div. min^{-1}. On putting off the light, however (pt. 'O' in Fig. 21), an almost immediate pressure-increase was observed, which had not reached completion after 65 mins. The rate of this pressure-increase fell off with time, and re-illumination (pt. 'L') then gave rise to a pressure-decrease which proceeded initially at a much greater rate (ca. 1.4 div. min^{-1}) than before the dark period. It will be shown later that illumination of TiO_2 in the presence of oxygen and hydrocarbon gives rise to oxidation of the latter, and it is concluded that the pressure-increase observed in this instance corresponded to desorption of products of the oxidation --- e. g. CO_2, H_2O etc.

Before proceeding to examine the kinetics of uptake on untreated TiO_2, a word should be said about the reproducibility of the results obtained. First, it should be remembered that two different samples of TiO_2 were used in the investigations. Although no serious differences were encountered between the behaviour of these preparations, each set of results has been labelled 'A' or 'B' (See P. 42) according to the sample used.

Large variations were, however, observed even within results obtained on different films of the same sample. It became apparent that the uptakes were particularly sensitive to the 'pre-treatment' given to the film - e. g. evacuation times and efficiency, presence or absence of irradiation prior to the uptake, etc. A systematic examination of the effect of pre-treating the TiO_2 surface in various ways will be presented in the following sections. It should further be remembered that although a standard weight of TiO_2 (0. 100 g.) was used in all the uptake experiments, this did not necessarily mean that the same surface area of oxide was exposed to the light-beam in all instances, this area being dependent on uniformity of film thickness. Finally, small fluctuations in light-intensity might also be responsible for influencing rates of uptake.

For a variety of reasons, therefore, quantitative reproducibility was difficult to achieve. In a more qualitative sense, however, the same pattern of behaviour was observable from film to film, and it is on this basis that most of the conclusions will be drawn.

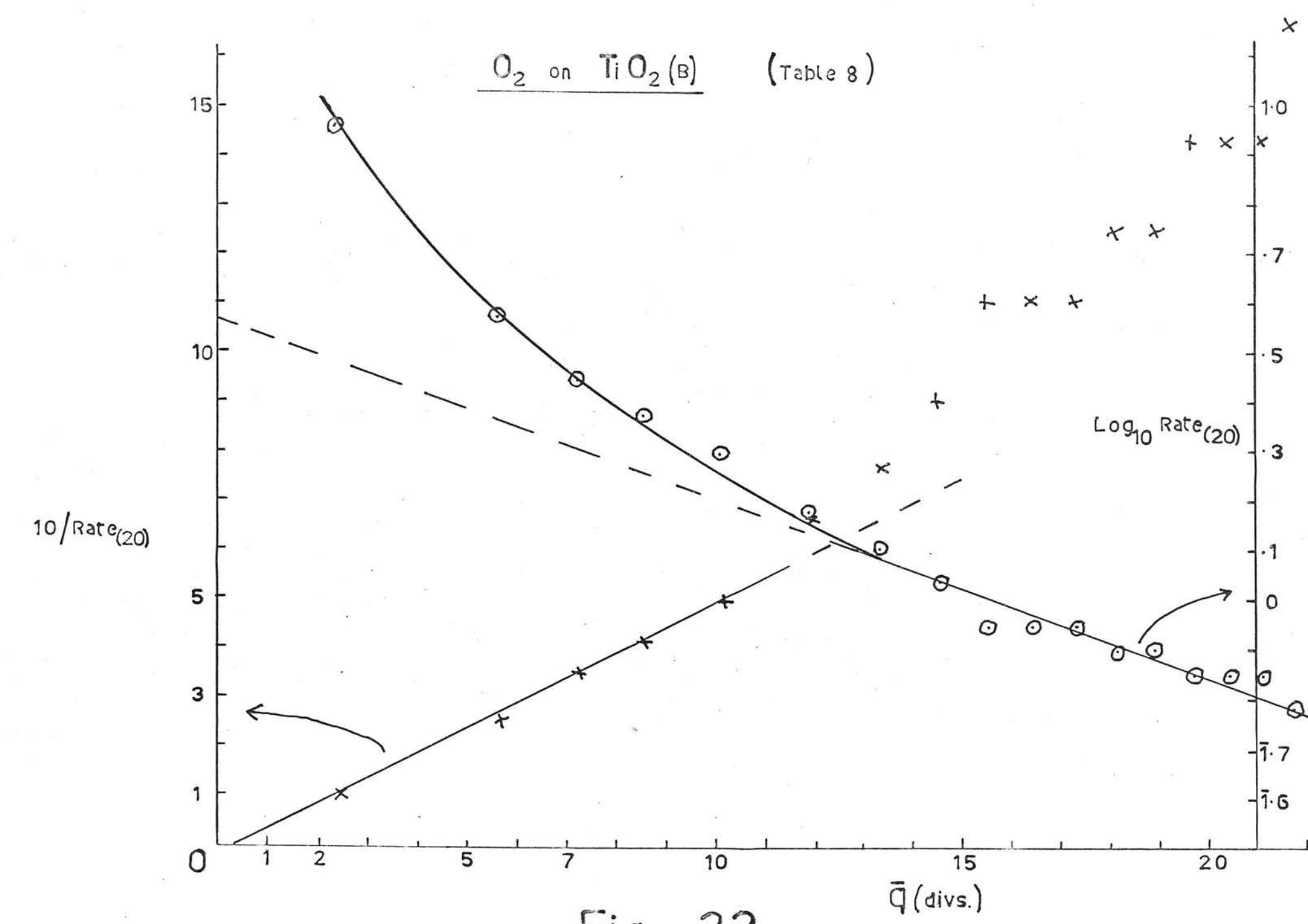

O_2 on TiO_2 (B) (Table 8)
10/Rate(20)
Log_{10} Rate(20)
$\bar{q}$ (divs.)
15
10
5
3
1
0
1
2
5
7
10
15
20
1·0
·7
·5
·3
·1
0
$\bar{1}$·7
$\bar{1}$·6

Fig 22

Kinetics of the uptakes.

The uptake kinetics were analysed in the way described in Experimental Sec. C, using primarily Rate $^{-1}$ vs $\bar{q}$ and $\log_{10}$ Rate vs $\bar{q}$ plots.

(A) Oxygen.

The kinetics of photouptake of O_2 were verified as being essentially 'parabolic' initially, reverting to Elovich in the later stages. The calculated rate data for the uptake represented in Fig. 14 (Table 1) are presented in Table 8, and the corresponding rate plots are illustrated in Fig. 22.

It can be seen that, in this instance, parabolic kinetics obtained up to q $\simeq$ 11 divs. (t $\simeq$ 60 mins.) and that a reasonably linear Elovich plot held after this time. Though the reciprocal-rate plot does not pass quite through the origin, the intercept (and hence qo) can be taken as effectively zero. The gradient of the line is 0.50, and using the relationship derived in Exptl. Sec. C, and remembering that we are here plotting 10/20. Rate, k = 2.0. Thus it can be said in this instance that, over the first 60 minutes, the uptake data obeyed the relationship, $q^2 = 2t$

Similarly, the gradient and intercept of the linear part of the log Rate plot are -0.0366 and 0.58 respectively, giving a = 0.19 and b = 0.08. The uptake data following 60 mins. of illumination

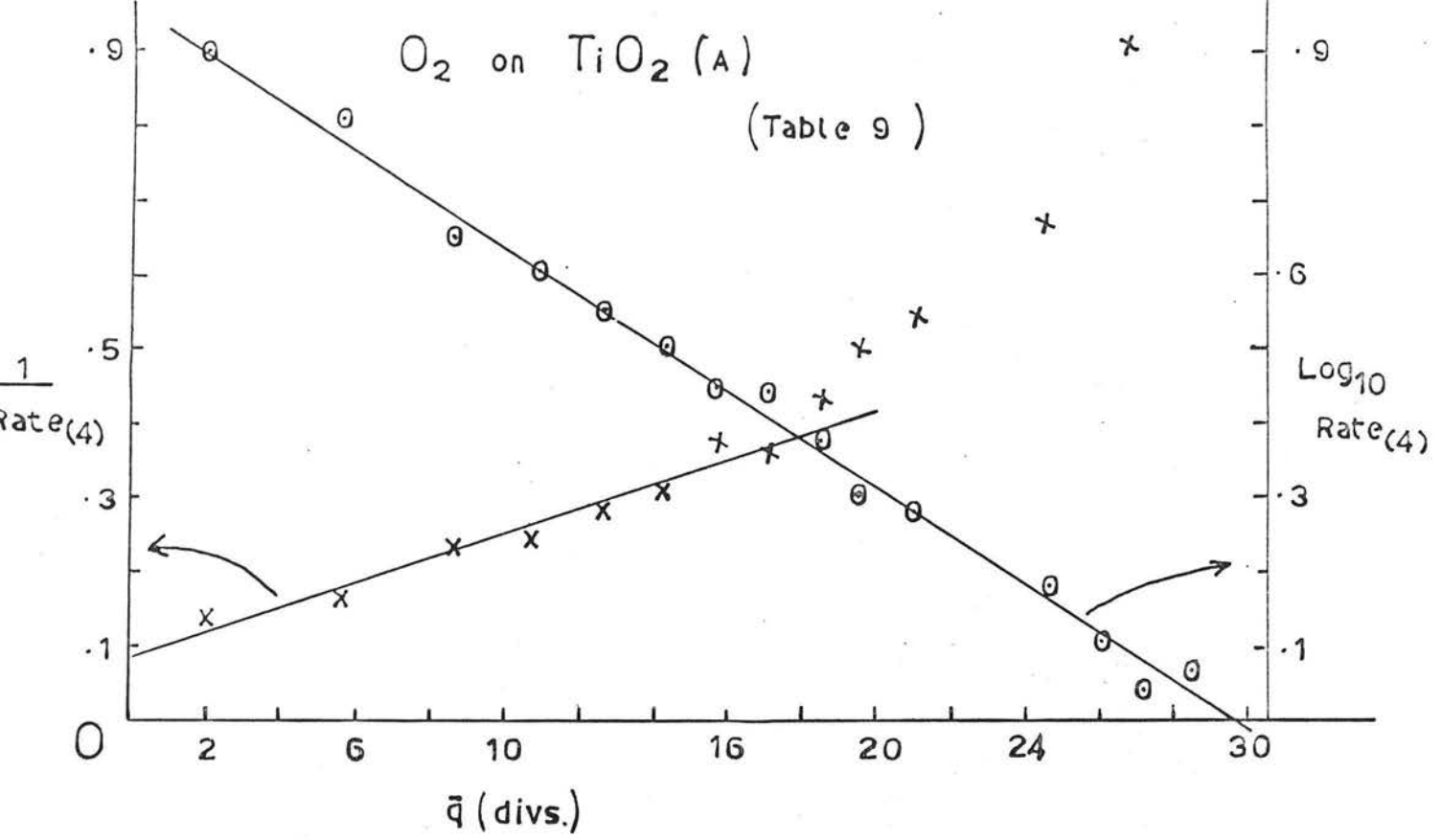


Fig 23A

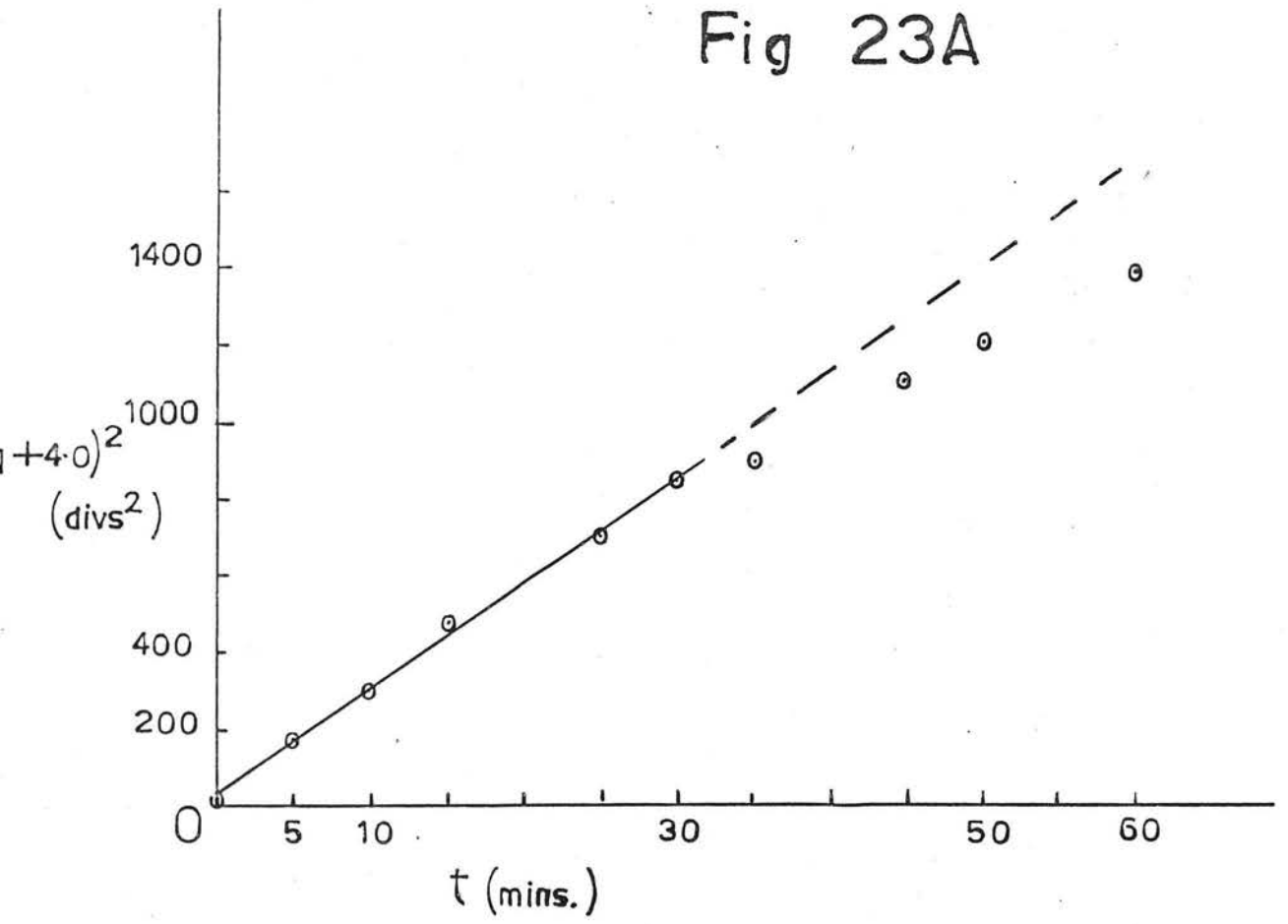


Fig 23B

C_2H_4 on TiO_2 (B) (Table 10)

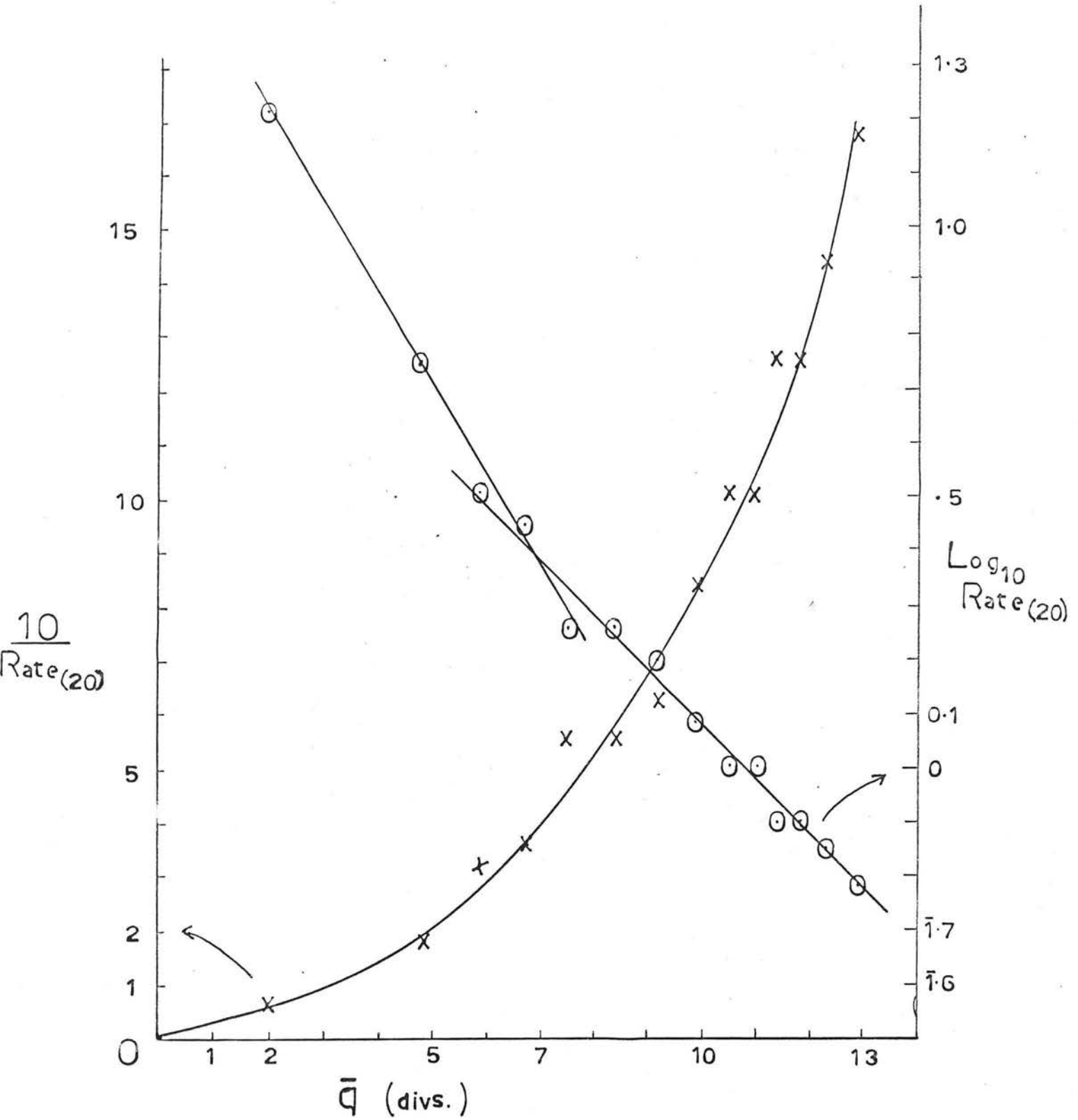


Fig 24

can therefore be represented by the Elovich expression

$$dq/_{dt} = 0.19\, e^{-0.08q}$$

In not all cases, however, was the issue quite so clear-cut as in the above example. For instance, the adsorption and rate-data of Table 9 gave rise to the plots shown in Fig. 23A. Here, it appeared that the parabolic and exponential relations held equally well up to $q \simeq 18$ ($t = 16$ mins). When the corresponding $(q + qo)^2$ vs t plot was constructed, however, this was seen to be linear, with $qo = 4$, up to $t = 30$ mins. (Fig. 23B). This uptake may then be said to be parabolic for the first 30 mins., and thereafter Elovich.

More will be said later (Discussion) about kinetic situations of this kind.

(B) Ethylene

The derived rate data for the C_2H_4 uptake represented in Fig. 14 are presented in Table 10, and are shown plotted in Fig. 24. It can be seen that this uptake could be represented by two Elovich lines, the break ocourring at approx. $t = 15$ mins. No parabolic section was here evident.

Marked non-reproducibility was, however, encountered in this connection - e. g. some uptakes did show a (small) parabolic section in the initial stages, some showed a fairly large parabolic section

except in the very early stages, and in some both the parabolic and Elovich relations appeared to hold simultaneously. In order to illustrate the divergency of results obtained, a selected number of uptakes, together with their observed kinetics, are presented below.

Film and TiO_2 sample	Kinetic relationships obeyed
1. (A)	Stage 1 - parabolic up to t = 30 mins., then Elovich up to t = 300 mins. Stage 2 - parabolic from t = 300 to t = 380, then Elovich.
2. (A)	Parabolic up to t = 8 mins., then Elovich; or, 2 Elovich lines.
3. (B)	Entirely parabolic; or Elovich after t = 6 mins.
4. (B)	2 Elovich lines up to t = 60; or, parabolic between t = 4 and t = 32.
5. (B)	No parabolic sec. 2 Elovich lines (break at t = 17); or, $q\frac{dq}{dt} = c - kq$ up to t = 25 mins.
6. (B)	No parabolic sec. 2 Elovich lines (break at t = 7)
7. (B)	Parabolic up to t = 30, then Elovich; or, Elovich after t = 6.
8. (B)	No parabolic sec. 2 Elovich lines (break at t = 15 mins.)

It should be remembered that complications existed here which were not present in the case of O_2. Viz -

(a) The small dark uptake, which could not be taken into account when examining the kinetics of the photo-process.

(b) The apparent initial rates must inevitably be lower than the true values, due to the heating effect of the light-beam, which acted in opposition to the uptake. In example 6 above, an attempt was made at correcting for this effect by noting the sudden pressure-decrease on cessation of illumination, and adding this quantity to each pressure-decrease value observed during illumination.

(c) Interruptions in illumination gave rise, as previously stated, to discontinuities in the uptake curves. The total uptake had thus to be split into 'stages' and each stage analysed separately from the others. --- see, e. g., example 1 above.

It may be noted from the above table that in practically every instance, Elovich kinetics described the uptakes even when a parabolic section could be fitted into the data, except perhaps in the very early stages. In addition, it was often found that the initial uptake could be best represented by a $q\frac{dq}{dt}$ vs q plot (e. g. film 5 above).

In general, however, it may be said that the kinetics of C_2H_4 photosorption have been shown to be characterised by Elovich

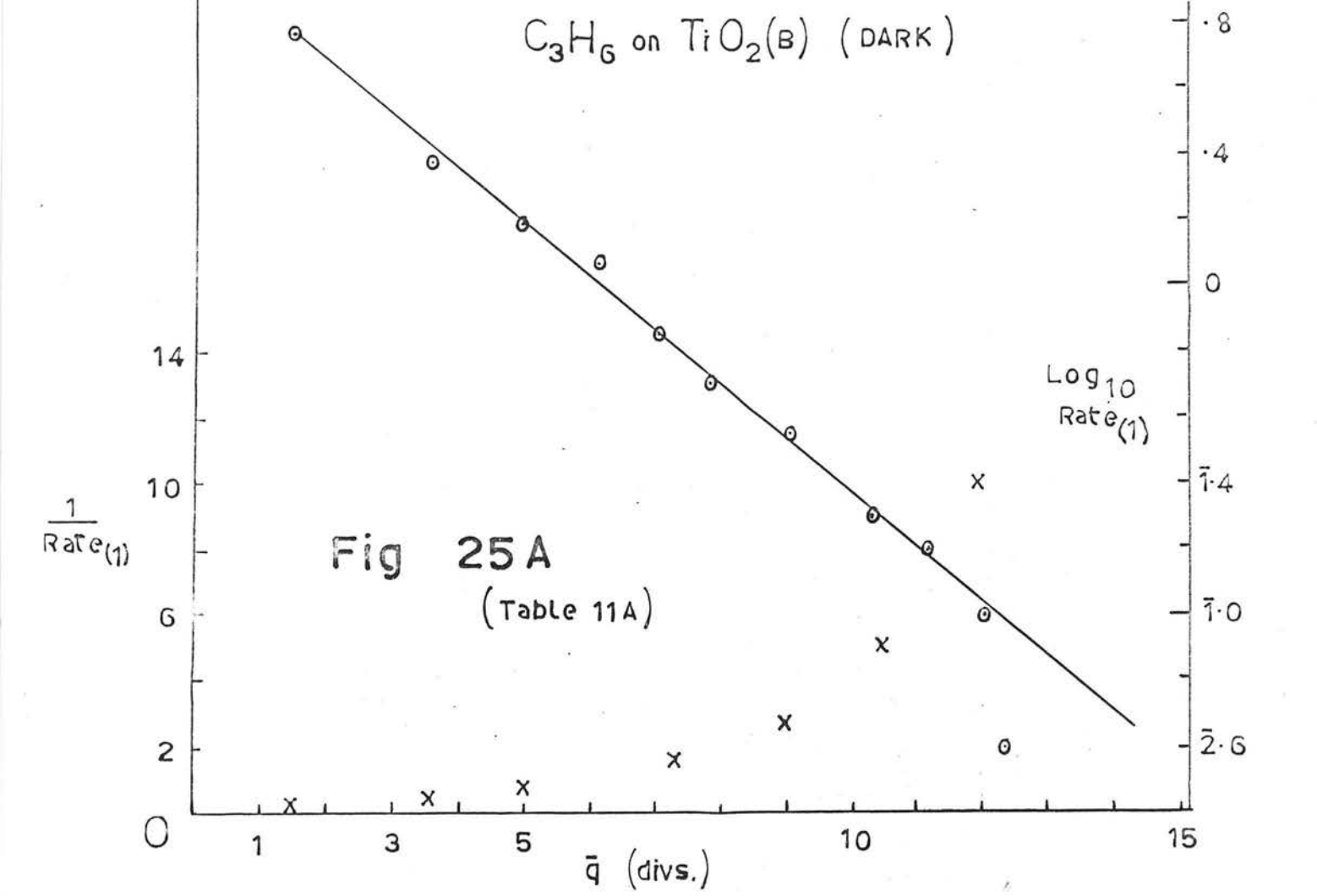


Fig 25A
(Table 11A)

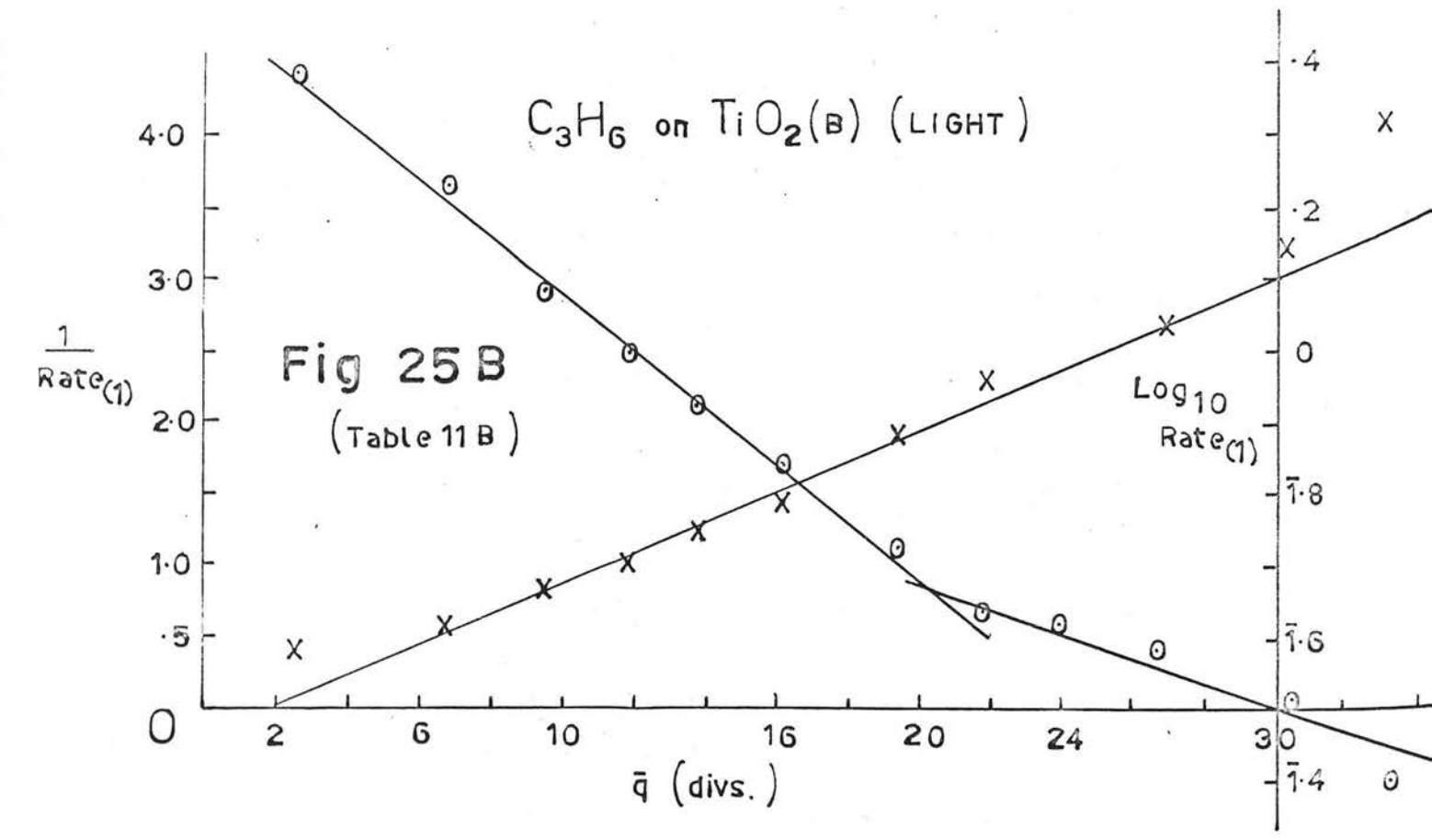


Fig 25B
(Table 11B)

expressions similar to those obtaining in the latter stages of O_2 - uptake.

(C) Propylene

Analysis of the C_3H_6 uptakes was complicated by the fact that the gas adsorbed in the dark. The general procedure adopted, therefore, was to allow the dark sorption to go to completion before irradiating the film, and to treat the two uptakes independently of one another.

For example, the uptake represented in Fig. 19 (Table 5) gave rise to the rate data presented in Tables 11A and B, which are plotted in Fig. 25A & B, respectively. It may be seen that the dark uptake obeyed Elovich kinetics over the whole of its course, except in the very last stages, when adsorption had virtually ceased. The light uptake, however, could be said to follow parabolic kinetics over most of its length, the first point in Fig. 25B no doubt lying off the line due to the heating effect of the light-beam. Again, it is to be noted that the kinetics could equally well be described by two Elovich lines, the break occurring after ca. 23 mins. illumination.

(D) Hydrocarbon/oxygen mixtures.

Due to the extremely rapid and extensive uptakes of these

mixtures, it was often virtually impossible to follow the pressure-decreases for long enough periods, and with sufficient accuracy, to permit kinetic analysis. In one experiment, however, the rates of uptake of a mixture of 15 mm O_2 : 43 mm C_2H_4 were low enough to follow the uptake with reasonable accuracy over 150 mins. In this instance, parabolic kinetics were followed up to $t \simeq 20$ mins., and one Elovich line sufficed to describe the rates over the remaining 130 mins.

The <u>dark</u> C_3H_6/O_2 uptake depicted in Fig. 20 was capable of being described by one Elovich line, except in the very late stages when the rates had fallen off practically to zero. Alternatively, a parabolic section could be fitted into the data over the first 25 mins. of uptake.

Pressure-dependence of the Uptakes

In order to examine the influence of the ambient gas-pressure on the rates of uptake, it was necessary to carry out measurements for each gas, or gas-mixture, on the same film. This was a consequence of the lack of quantitative reproducibility encountered from film to film at this stage. The procedure adopted, therefore, was to carry out adsorption measurements in the usual way for a short length of time at a given pressure, and then to step up the pressure by the required amount by admitting more gas to the reaction-system, with no break in illumination. Since this could not be accomplished instantaneously, the uptake curve constructed for the lower pressure data was extrapolated to a point 1 min. (the time generally required to complete the pressure-increase) in advance of the last reading, and subsequent pressure decreases calculated accumulatively from this value. This procedure could be repeated on the same film indefinitely.

Comparison of rates immediately prior to, and following, the pressure-increases provided some information on their pressure-dependence. Ideally, some form of extrapolation of rate-values was obviously desired. However, due to the uncertainty in the kinetics, and also for reasons which will become apparent later, this procedure proved unsuccessful.

O_2 uptake — Pressure dependence

(Table 12)

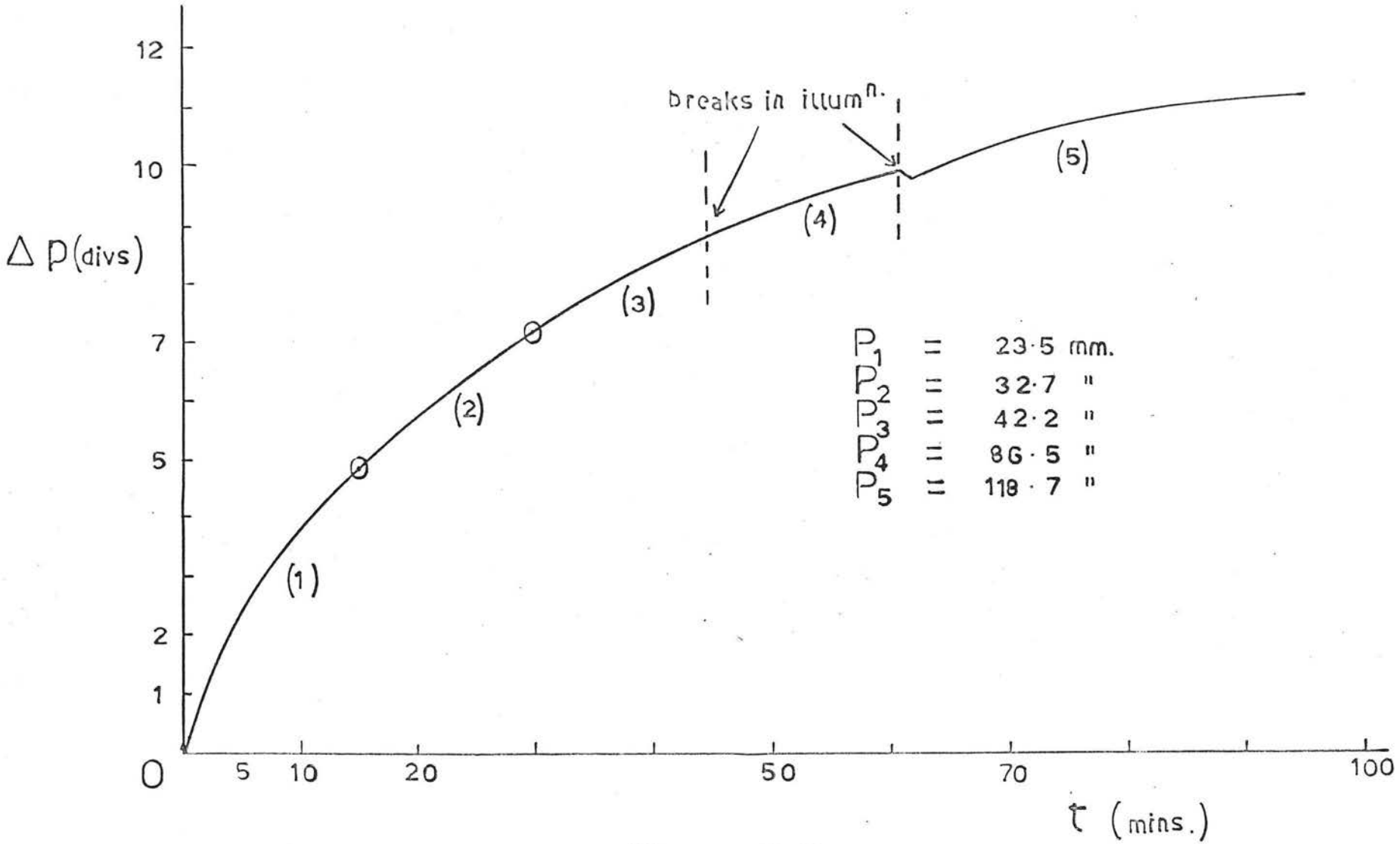


Fig 26

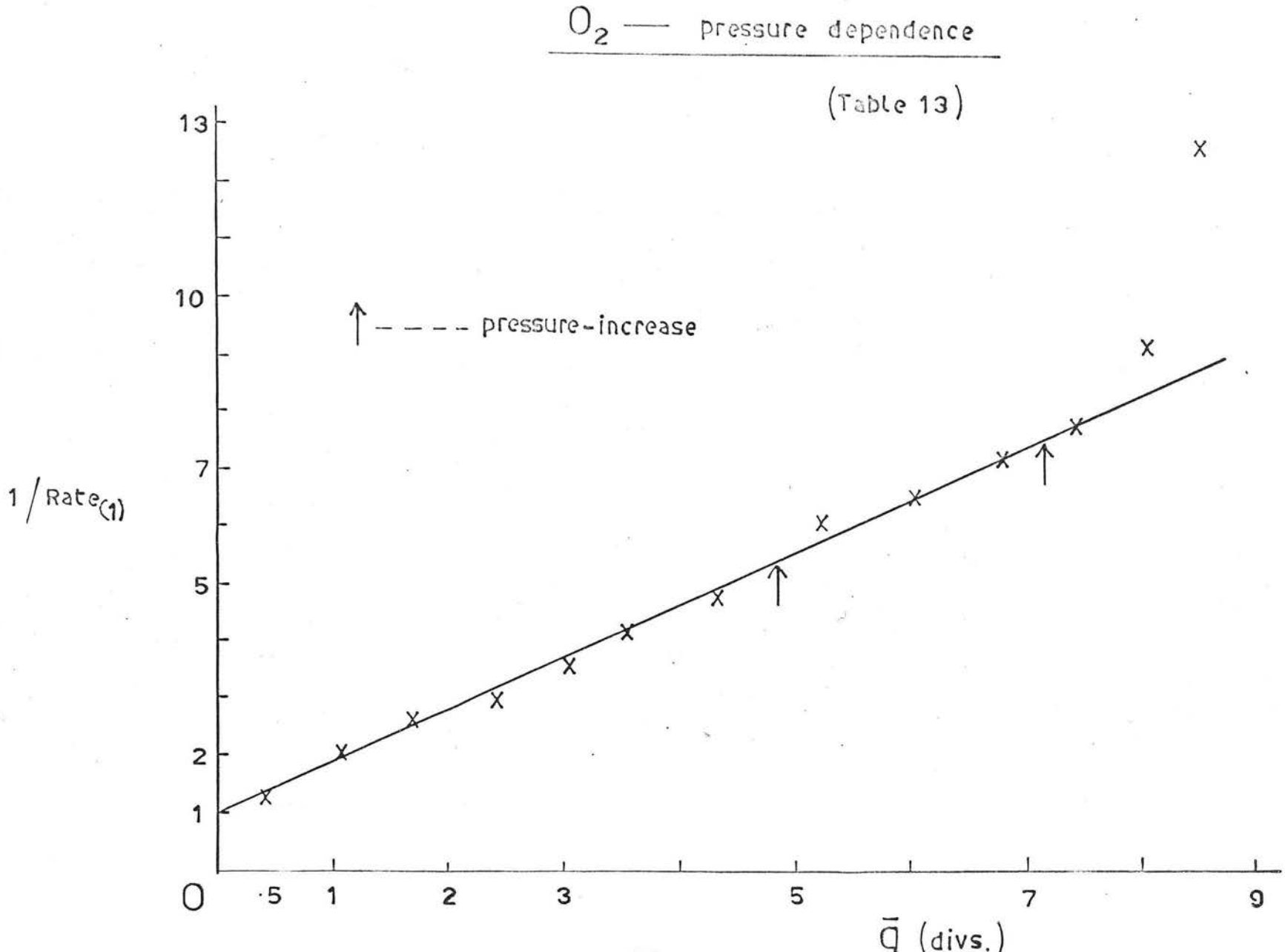

O_2 — pressure dependence
(Table 13)
13
10
7
5
2
1
0
·5
1
2
3
5
7
9
↑ - - - - pressure-increase
1 / Rate(1)
q̄ (divs.)

Fig 27

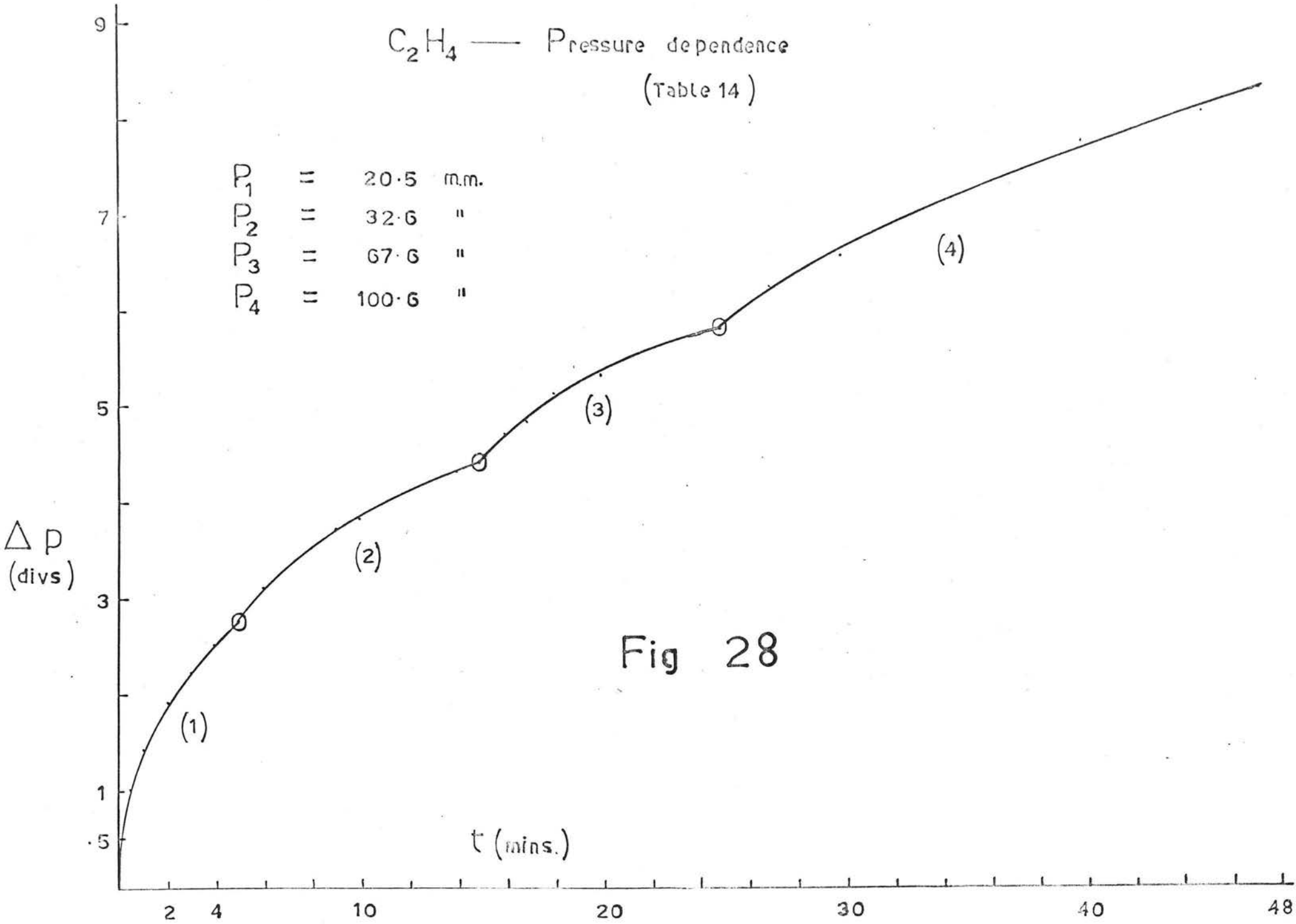

C_2H_4 — Pressure dependence
(Table 14)
P_1 = 20·5 m.m.
P_2 = 32·6 "
P_3 = 67·6 "
P_4 = 100·6 "
Δ p (divs)
t (mins.)
(1)
(2)
(3)
(4)
9
7
5
3
1
·5
2
4
10
20
30
40
48

Fig 28

(A) Oxygen

Fig. 26 (Table 12) shows the effect of four pressure-increases on a typical O_2 uptake over 96 mins. illumination. (The points enclosed by circles indicate extrapolated Δp values). It can be seen that no discontinuities are observable up to t = 61 mins. - the small pressure increase on re-illumination at this point is no doubt due to thermal effects which have become significant at the high pressure. Fig. 27 (Table 13) shows a reciprocal-rate plot of the same data over the first 45 mins. Again, no discontinuities are observable, though the pressure has been raised twice during this time.

It is to be concluded from these results that, under the above conditions, and within the pressure-range studied, no significant pressure-dependence was displayed by the O_2-uptakes.

(B) Ethylene

In contrast with the results obtained in (A), the C_2H_4 photo-uptake was observed to show a fairly marked positive pressure-dependence. Fig. 28 (Table 14) shows the effect of three pressure-increases over 60 mins., and the corresponding rates before and after the pressure-rises are compared below.

t(mins)	P(mm)	Rate(div/min)	$Rate_{n+1}/Rate_n$	P_{n+1}/P_n
4	20.5 (1)	0.25		
(5)			(2)/(1) = 1.4	1.6
6	32.6 (2)	0.35		
14		0.10		
(15)			(3)/(2) = 2.5	2.1
16	67.6 (3)	0.25		
24		0.10		
(25)			(4)/(3) = 2.0	1.5
26	100.6 (4)	0.20		

In the above table, the 'rates' quoted are simply the differences between the extrapolated Δp values and the recorded values 1 min. before, and 1 min. after, the corresponding pressure-increases. Times enclosed in brackets are those corresponding to the extrapolated Δp values.

It can be seen that the ratios of the rates are in all cases of roughly the same magnitude as the corresponding pressure-ratios. (It should be stressed, however, that it did not follow that the rates as measured over any length of time bore this relationship. In fact, the mean rates, taken over the entire period of measurement for each pressure, decreased for successive pressure-

C_2H_4 sorption rates at different pressures
□ ..... 20·5 mm.
△ ..... 32·6 "
○ ..... 67·6 "
X ..... 100·6 "
1·8
1·3
1·0
·7
·5
·2
·1
0
·5
1
2
5
7
$\frac{1}{\text{Rate}}$
$\bar{q}$

Fig 29

C_3H_6 (DARK) —— three pressure increases

(Table 15 A)

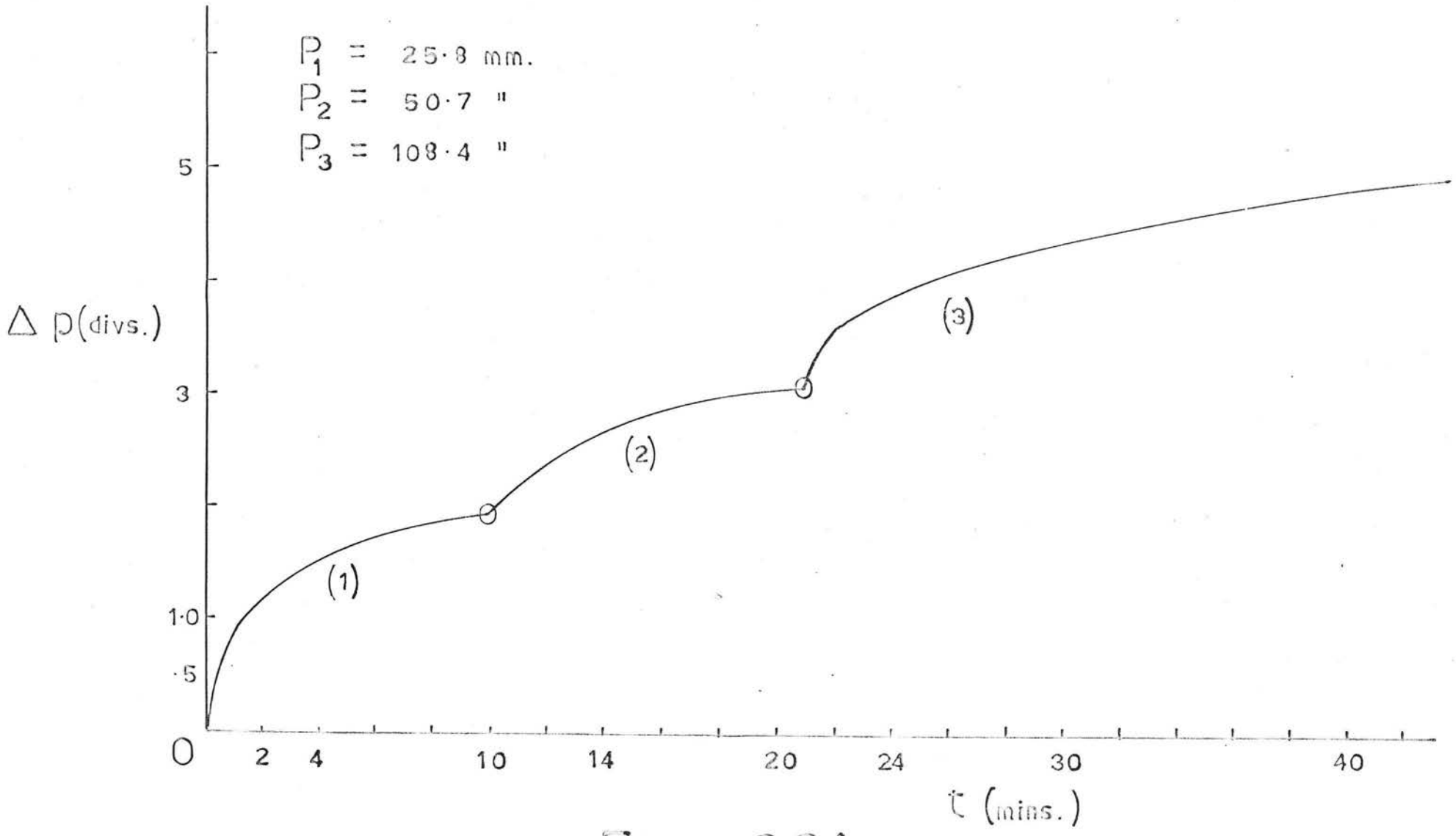


Fig 30A

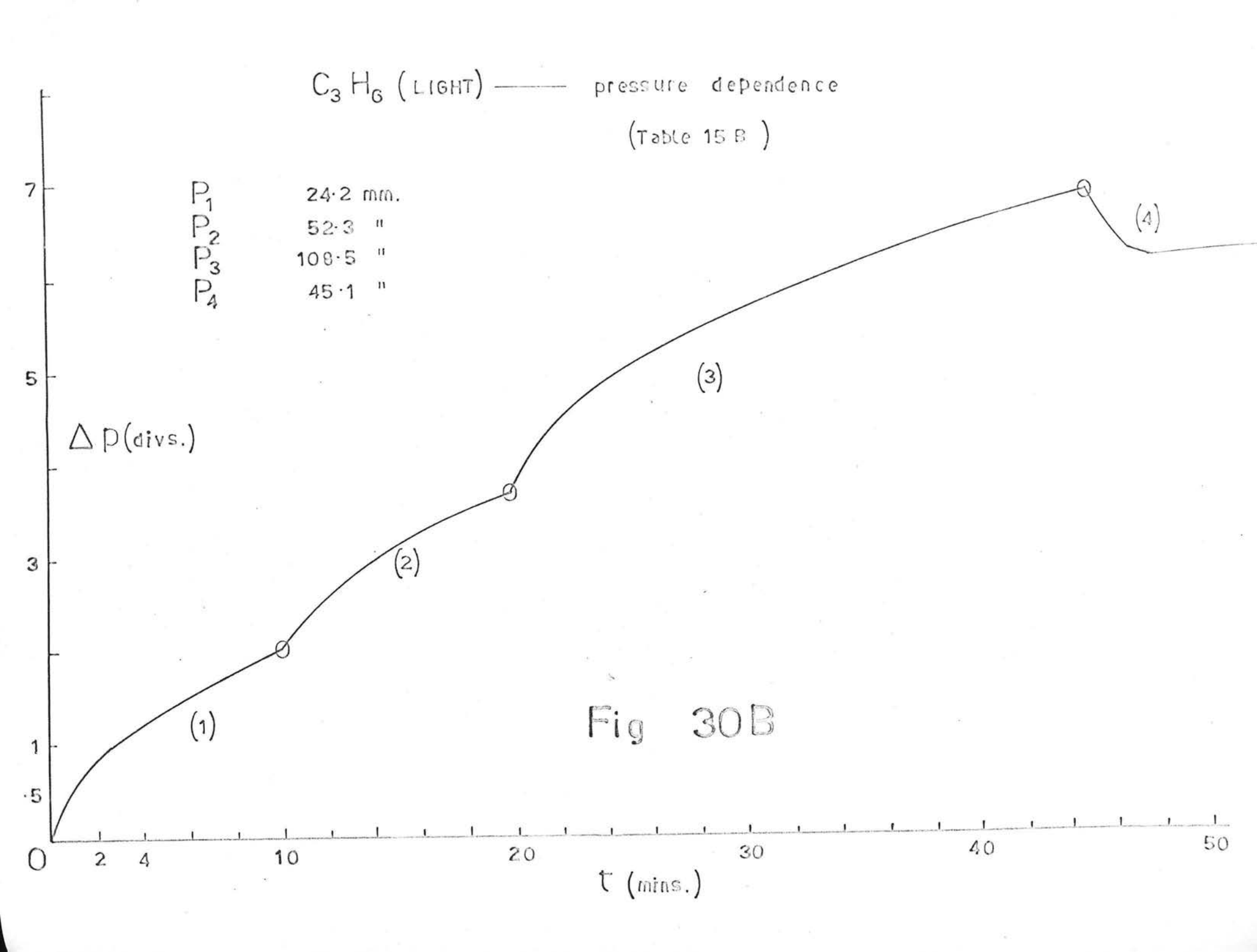

C3 H6 (LIGHT) —— pressure dependence
(Table 15 B)
P1 24·2 mm.
P2 52·3 "
P3 108·5 "
P4 45·1 "
Δ p(divs.)
7
5
3
1
·5
0
2
4
10
20
30
40
50
t (mins.)
(1)
(2)
(3)
(4)

Fig 30B

increases).

An attempt was made at constructing reciprocal-rate plots for each section of the uptake curve represented in Fig.28, in the hope that suitable linear extrapolations could be made in order to obtain more accurate data for comparison. These plots are illustrated in Fig. 29, and it can be seen that the points fall onto four distinct lines, each representing a different pressure. However, each line has a different gradient, and it is difficult to see what legitimate comparison of results can be made in these circumstances. Indeed, in view of the kinetic results given earlier, it is doubtful whether any extrapolation of data of the above kind is justified.

An alternative approach to the problem is presented at the end of this section.

(C) Propylene

Both the dark and light uptakes of C_3H_6 were found to be influenced by changes in pressure (Tables 15a & b and Figs 30a & b) in a way similar to that of C_2H_4. The photouptake was examined by allowing the initial dark sorption to go to completion before illumination, as usual. However, the observed pressure-dependence of the latter uptake makes any quantitative interpretation of the subsequent rate-increases difficult.

(D) Hydrocarbon/oxygen Mixtures

No discontinuities were observed in the photo-uptake curves of C_2H_4/O_2 and C_3H_6/O_2 mixtures when the O_2-pressure was varied between 25 and 80 mm., keeping the olefin-pressure constant at approx. 30 mm. This is in agreement with the lack of pressure-dependence displayed by pure O_2-uptakes.

The uptake of a C_2H_4/O_2 mixture was found, however, to show a positive dependence on the C_2H_4 partial pressure when this was varied from 22 mm. to 106 mm., the O_2-pressure being constant at 17 mm.

Vid:-

$P C_2H_4$ (mm.)	Rate over last min. prior to P-increase (divs. min.$^{-1}$)	Rate over first min. following P-increase (divs. min.$^{-1}$)	P-ratio	Rate-Ratio
22.0	1.0			
54.3		2.5	2.5	2.5
	1.0			
75.5		1.5	1.4	1.5
	0.85			
105.5		1.1	1.4	1.3

It can be seen from the above Table that there is surprisingly

C_3H_6 / O_2 — C_3H_6 pressure varied

O_2 P = 23·6 mm.

C_3H_6 P_1 = 20·5 "

P_2 = 47·3 "

P_3 = 70·9 "

P_4 = 88·7 "

(Table 16)

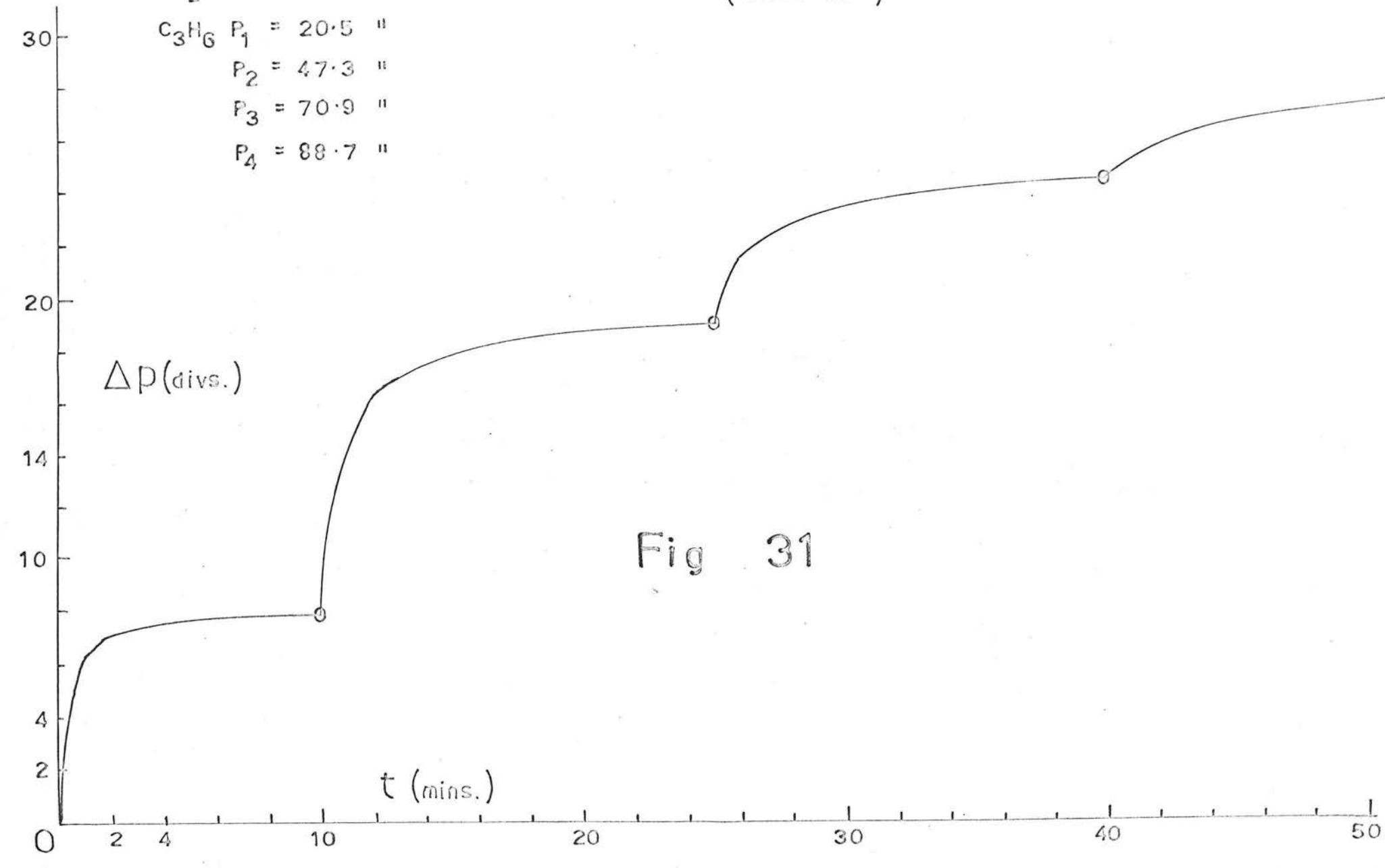


Fig 31

good agreement between the pressure-ratios and the ratios of the rates immediately before and after the pressure-rises.

C_3H_6/O_2 dark uptakes were found to show a striking dependence on the C_3H_6 pressure. Fig. 31 (Table 16) shows the effect of three increases in the C_3H_6 pressure, holding the O_2 pressure constant at 23.6 mm. As can be seen, the uptake was extremely rapid immediately following a pressure-rise, but died off equally rapidly, and practically to zero rate, after only ca. 15 mins.

In contrast, the photo-uptake of a C_3H_6/O_2 mixture was found to display little dependence on the C_3H_6 pressure, at least in the early stages, e.g. (O_2 pressure const. at 23.6 mm.)

P C_3H_6 (mm.)	Rate prior to P-increase (divs.min^{-1})	Rate following P-increase (divs.min^{-1})	P-ratio	Rate-ratio
28.2	1.8			
50.7		1.6	1.8	0.9
	1.2			
88.1		2.1	1.7	1.7

General

Although in many of the examples quoted there is a surprising degree of comparison between the pressure-ratios and the ratios of

the corresponding 'rates' before and after the pressure-increases, it is felt that such relationships may be largely fortuitous. No account is taken of coverage, and the results are entirely dependent on the time-range over which the rates are computed.

In many ways it seemed more legitimate to compare the initial rates following the pressure-increases, as these regions of the uptake curve appeared to be particularly pressure-sensitive. The evidence of Fig. 29 suggested that within the early stages of each uptake-section the rates were inversely proportional to the uptake at that time. Assuming a simple pressure-relationship of the type

$$\text{Rate} \propto P^x$$

it seemed reasonable to examine the applicability of an expression

$$dq/dt = k.\frac{P^x}{q}$$

to the very earliest stages of each section of the uptake curve. If these sections are labelled 1, 2.....n, with corresponding pressures P_1, P_2.....P_n mm., initial rates (over the first min.) $(dq/dt)_1$, $(dq/dt)_2$..... etc. and mean uptakes over the minute interval $\bar{q}_1$, $\bar{q}_2$.....$\bar{q}_n$, the above relation gives rise to

$$\frac{(dq/dt)b}{(dq/dt)a} = \frac{(P_b)^x}{(P_a)^x} \cdot \frac{\bar{q}a}{\bar{q}b}$$

and $$x = \frac{\log.\ (\text{Rate b/Rate a}) - \log.(\bar{q}_a/\bar{q}_b)}{\log.\ (Pb/Pa)}$$

This computation was carried out for all combinations of a and b, for the C_2H_4 photo-uptake of Fig. 28 and the C_3H_6 dark uptake of Fig. 30A. The results are presented in Table 17.

It can be seen that good agreement was obtained between the calculated x - values for the C_2H_4 photosorption, though the C_3H_6 values are more badly scattered. It may, then, be said that, for these two uptakes, the initial rates may be represented by

(1) $$dq/dt = k_e \cdot \frac{P^{0.12}}{q} \qquad \text{for } C_2H_4 \text{ (light)}$$

and (2) $$dq/dt = k_p \cdot \frac{P}{q} \qquad \text{for } C_3H_6 \text{ (dark)}$$

These expressions do not hold except in the earliest stages following a pressure-increase.

No attempt was made to treat the C_3H_6 photo-uptake in a similar way, owing to the complications of the dark pressure-dependence. Preliminary calculations did show, however, that the rate-increases were greater than expected on the basis of equation (2) above, indicating that the photo-uptake was also subject to a positive pressure coefficient.

II. Uptake of hydrocarbon and oxygen on hydrocarbon and oxygen - treated films.

The effect of carrying out successive adsorptions of the same gas on the same TiO_2 film has already been mentioned in Sec. I.

C_2H_4 and C_3H_6 uptakes on C_3H_6 and C_2H_4 - treated films, respectively, were given a cursory examination in order to verify what seemed highly likely - that both olefins utilised some, or all of, the same surface sites during photo adsorption. The results of two experiments of this type appeared to bear this out:-

(1) A film was illuminated in 42 mms C_3H_6 for 30 mins., following the usual dark uptake, and during this time took up 13 divs. (sensitivity 0.018 mm div.$^{-1}$) of C_3H_6. The film was then evacuated overnight, and a normal C_2H_4 sorption carried out. After the usual small dark sorption (ca. 3 divs), illumination led to the further uptake of only 3.4 divs. in 30 mins. This is to be compared with the uptake of C_2H_4 observed on a previous, untreated film of 28 divs. in 30 mins., at the same sensitivity.

(2) A film was illuminated in 49 mms C_2H_4 overnight. The total amount of C_2H_4 photosorbed was indeterminate, but the uptake after 144 mins. was 13.3 divs (sens. 0.050 mm/div). After three hours evacuation, C_3H_6 was admitted, the dark uptake allowed to go virtually to completion, and the film illuminated.

The dark pressure-decrease was of the same order as that expected for an untreated film (3. 3 divs in 30 mins.), but after 50 mins. illumination only a further 1. 7 divs had been taken up.

It was thus established that the pre-adsorption of one hydrocarbon markedly reduced the rate and extent of uptake of the other, though the dark sorption of C_3H_6 did not appear to be significantly affected by the presence of adsorbed C_2H_4. The indication was that pre-sorption of C_3H_6 was more effective in reducing the subsequent uptake of C_2H_4, than vice-versa.

In contrast, the pre-adsorption of O_2 greatly enhanced the subsequent uptake of both C_2H_4 and C_3H_6, and, similarly, O_2 was taken up in greater amounts by films pre-treated with hydrocarbon. In one experiment, for example, the C_2H_4 uptake over 1 hour's illumination was almost doubled by pre-sorbing O_2. For convenience, results of this kind which are considered to be typical are presented in the table below. In order to standardise the uptakes, they are all expressed in units of gauge divisions, sensitivity 0. 050(3) mm div^{-1}.

Pre-sorption	Gas	Uptake after 'n' mins., Δp_n (divs)
-	O_2	$\Delta p_{60} = 11.5$
15.0 divs C_2H_4	"	$\Delta p_{60} = 15.4$
7.9 divs. photosorbed C_3H_6	"	$\Delta p_{45} = 26.3$
-	C_2H_4	$\Delta p_{60} = 9.0$
11.5 divs O_2	"	$\Delta p_{60} = 17.5$
-	C_3H_6	Dark $\Delta p_{30} = 3.8$ ($\Delta p_{10} = 3.4$)
		Light $\Delta p_{15} = 12.4$ ($\Delta p_{15} = 6.5$)
26.3 divs O_2	"	Dark $\Delta p_{10} = 44$
		Light $\Delta p_{15} = 7.5$

The most striking features of the above table are, perhaps, the large increase in O_2 - uptake on a C_3H_6 - treated film, and the very great increase in the C_3H_6 dark sorption caused by presorption of O_2. The dark C_2H_4 uptake was not increased by the presence of adsorbed O_2; nor was O_2 itself adsorbed in the dark on a hydrocarbon -treated surface, in quantities sufficient to be detected by the meter.

Though oxidation may be occurring in the above instances, no evidence was obtained for this - i. e. no appreciable CO_2 or other

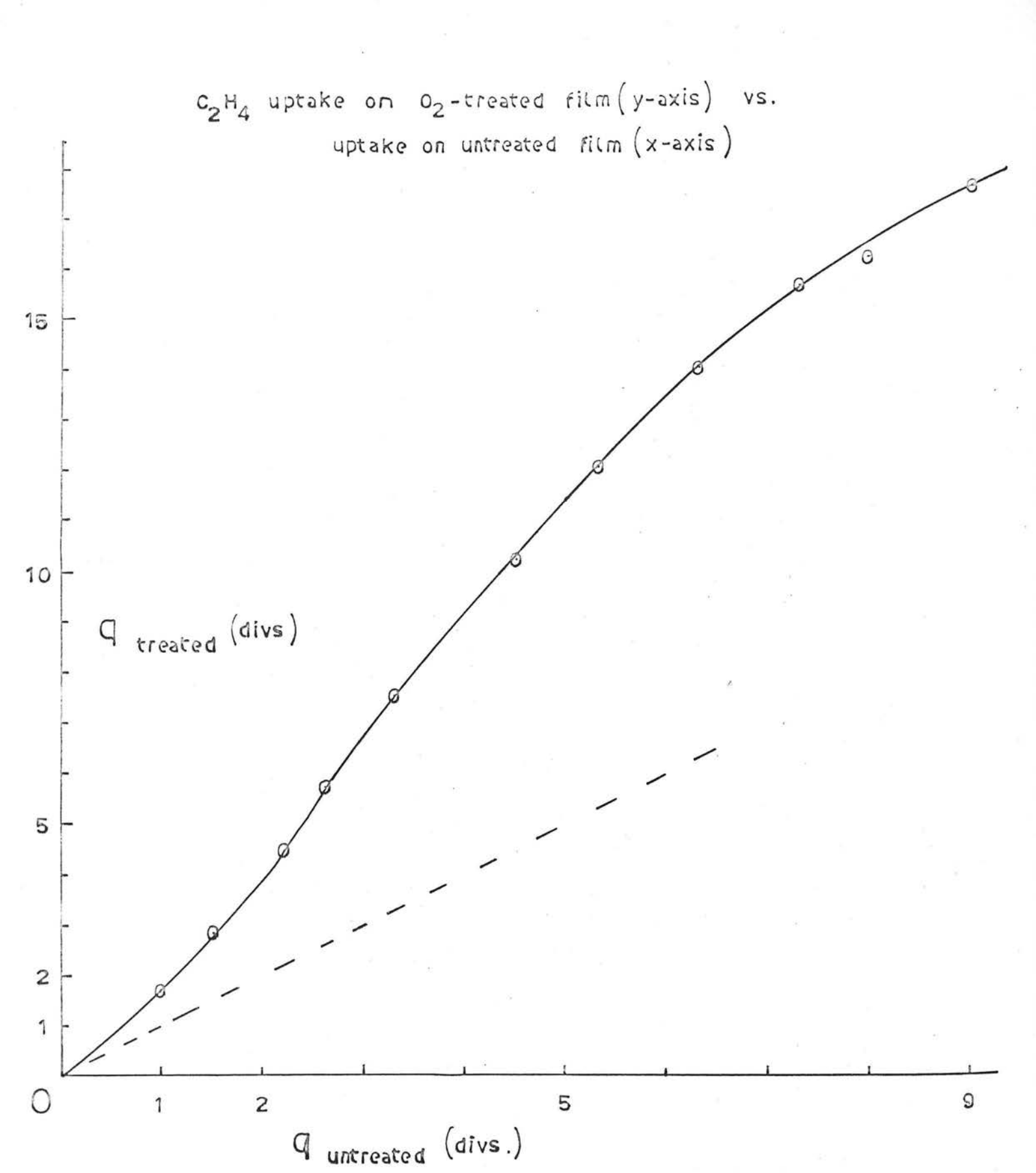

C_2H_4 uptake on O_2-treated film (y-axis) vs.
uptake on untreated film (x-axis)
15
10
5
2
1
0
q treated (divs)
1
2
5
9
q untreated (divs.)

Fig 32

possible oxidation product was recovered on pumping the films through a cold-trap following the uptakes.

The exact way in which pre-adsorption of O_2 affected a subsequent C_2H_4 uptake during its course, is shown in Fig. 32, in which the uptake is plotted against a corresponding uptake on an untreated film.

The kinetics of uptake on such pre-treated films were similar in form to those holding for the untreated cases.

III. Uptakes on Cl^-, OH^-, Na^+ and H^+ - treated films

The precipitation of TiO_2 in saline solution must inevitably leave the surface contaminated with chloride, sodium, hydroxide and, possibly, hydrogen ions, despite the neutralisation and washing procedures outlined on P. 43. There is also the possibility of incorporation of these ions within the oxide lattice.

The investigation of Woods and Wright (69) into the semiconductivity of CdS crystals showed that the effect of incorporating chloride into the lattice was to create electron-traps below the conduction band. Thus it seemed possible that surface, or lattice chloride might be involved in the uptakes on TiO_2. Similarly, the possibility of involvement of surface hydroxyls in the O_2 uptakes has already been mentioned (Introduction Secs. III & VII). Yates and Lucchesi (83) suggest that surface OH's may play a part in the observed chemisorption of C_2H_4 on γ - irradiated SiO_2. These authors further obtained evidence that surface sodium was involved in the C_2H_4 uptake on unirradiated samples. MacLean (3) introduced the concept of Lewis-acid type centres on the TiO_2 surface, where absorption of a light-quantum led to the production of H^+ ions, which were considered to be utilised in the formation of H_2O during O_2 sorption. It was also thought possible by the present author that species such as H^+, H_2O^+ or H_3O^+ might be

involved in the hydrocarbon uptakes.

For the above reasons, therefore, it seemed logical to examine the effect on the various uptakes, of pre-treating the surface with NaCl, NaOH, and various acids.

It should be emphasised, however, that any results quoted in this section are wholly concerned with surface (i. e. adsorbed) impurities, and cannot be taken as providing information on the effect of incorporating these impurities within the lattice.

Determination of chloride.

An estimation of the chloride-content of a typical TiO_2 sample was obtained by boiling a suspension of the oxide in c on c. H_2SO_4, and passing the HCl evolved into NaOH soln. The turbidity resulting from the addition of $AgNO_3$ to the acidified solution was compared with that obtained from a series of standard chloride solutions. In this way an estimate was made of the upper limit to the chloride concentration in the original sample.

Two determinations were carried out, (a) by the author and (b) by Vickerman (19) in this Department. It was found that the turbidity resulting from 0. 1000 g TiO_2 corresponded to not more than:-

(a) 0. 0006 g NaCl and (b) 0. 0003 g NaCl

i. e. $(Cl^-) \not> 0.004$ g/g TiO_2 i. e. $(Cl^-) \not> 0.002$ g/g TiO_2

i. e. mean $(Cl^-)_{max}$ = 0.003 g/g TiO_2

which corresponds to 84 μmoles Cl^- /g TiO_2

In order to compare this value with the molar quantities involved in a typical uptake, let us consider an uptake of 25 divs. at sensitivity0.050(3) mm/div. on 0.100 g TiO_2 at 27°C. (This figure is somewhat greater than the uptake of O_2 normally encountered after ca. 300 mins. illumination on untreated TiO_2). Recalling that the reaction-volume was approx. 58 mls, this corresponds to

$$\frac{58 \times 25 \times 503 \times 273}{224 \times 760 \times 300}\ \mu\text{moles gas} = 3.9\ \mu\text{moles}$$

or, 39 μmoles /g TiO_2

Thus, in molar terms, the concentration of chloride (or sodium) is of the same order of magnitude as the gas uptakes.

A series of uptakes were carried out on films pre-treated with NaCl, NaOH & HCl solns, HCl gas and oxalic acid dihydrate soln. Solids (and HCl) in solution were deposited on the TiO_2 surface in the manner described on P. 47, in quantities given in the table below.

HCl gas was prepared by adding conc. H_2SO_4 to NaCl in vacuo, and was purified by distillation. It was found that the gas adsorbed greatly within the cell, making it impossible to assess accurately the amounts taken up, and/or retained after pumping, on the film.

Further, it was found that leaving a film in contact with the gas for long periods (> ca. 5 hrs.) led to disintegration of the film. The procedure generally adopted, therefore, was to admit the HCl directly to the cell and reaction-vessel, leave the film in contact with the gas (P~40 mms) for ca. 1 hour, and then pump the film extensively (e. g. overnight) before examining a subsequent hydrocarbon-uptake. Normally, re-expansion of the HCl following an experimental run indicated that approximately 5 mms of the gas had been retained by the TiO_2, and an aqueous extract of the film was always acid to litmus.

In the table below, all the uptakes were carried out on 0. 100 g TiO_2 (B) and are expressed in gauge divs., sensitivity 0. 050(3) mm. div^{-1}.

Gas	Pre-treatment	Uptake after 'n' mins., q_n (divs)
C_2H_4	50 μmoles NaCl	q_{10} = 3. 0, q_{30} = 4. 5
	50 μmoles NaOH	q_{10} = 4. 0, q_{30} = 6. 2
	2 μmoles HCl(soln)	q_{10} = 5. 0, q_{30} = 7. 2, q_{60} = 8. 5
	? μmoles HCl(gas)	q_{10} = 1. 0, q_{25} = 2. 4
	5 μmoles $H_2C_2O_4 \cdot 2H_2O$	q_{10} = 3. 7, q_{120} = 8. 0
	25 μmoles $H_2C_2O_4 \cdot 2H_2O$	q_{10} = 1. 4, q_{55} = 2. 3

C_3H_6	2 μ moles HCl(soln.)	Dark	$q_{30} = 3.4$	
		Light	$q_{10} = 2.2$,	$q_{60} = 5.3$
	? μ moles HCl(gas)	Dark	$q_{10} = 8.0$	
		Light	$q_{30} = 1.0$	
	5 μ moles $H_2C_2O_4$	Dark	$q_{30} = 3.2$	
		Light	$q_{56} = 3.0$	
	25 μ moles $H_2C_2O_4$	Dark	$q_{30} = 2.6$	
		Light	$q_{25} = 1.3$	
O_2	5 μ moles $H_2C_2O_4$		$q_{60} = 9.5$	$q_{140} = 14.1$

Notes.

(1) The effect of pre-treating the surface with NaCl on the O_2 uptakes has previously been examined by Vickerman (19), who found no evidence for any relationship between the amount of chloride placed on the film, and the extent of the uptake. He did, however, suggest that the kinetics were modified in some way.

(2) It may be noted from the above table that the C_2H_4 photo- & C_3H_6 dark uptakes on HCl (soln.) - treated TiO_2 were normal in extent, though the C_3H_6 photosorption was smaller than usual. The validity of these results is, however, questionable, since it is likely that much, if not all, of the HCl placed on the surface

was removed by subsequent pumping. In fact, one film, following a C_2H_4 uptake, was extracted with 2 x 1 ml. H_2O, and the solution found to have an approx. pH of 9.0. An equal weight of TiO_2 blank extracted in the same way gave a solution of pH approx. 8.5. The same problem was present in the case of treatment with HCl gas, and, additionally, it was not known to what extent the HCl was dissociated on the surface. It was for these reasons that oxalic acid was chosen, in order to provide more accurate information on the surface proton-concentration, this acid being water-soluble and having a negligible vapour-pressure.

(3) In addition to the above, it was possible that the oxalic acid might be oxidisable by photoadsorbed O_2.

In order to test this possibility, 5 μ moles $H_2C_2O_4 . 2H_2O$ were placed on a film which was evacuated in the usual way for ca. 30 mins. After this time, the film was pumped through the cold-trap situated between T_9 and T_{10} for 17 hours. A rough vapour-pressure analysis was then carried out by expanding the trapped-out vapours into the right side of the Bourdon guage (i.e. with T_2 closed), the cell being isolated. The trap was found to contain 2 divs CO_2 + 53 divs H_2O. These vapours were then pumped from the system, and the film illuminated in vacuo for 6 hours. No pressure-changes were recorded during this time. Further

pumping through the cold-trap (21 hours) following the illumination produced 1.5 divs CO_2 + 34.5 divs H_2O.

After again removing the vapours, 45 mm O_2 was admitted to the film, and the system illuminated for 140 mins., after which time 14.1 divs had been photosorbed (see Table). (The kinetics of this uptake could be described by a parabolic expression over the first 60 mins., but an Elovich plot fitted the data equally well after 25 mins.). Following the uptake, the film was repumped through the cold-trap (18 hrs.), and yielded a further 2 divs CO_2 + 39 divs H_2O.

It was thus evident that no appreciable photo-oxidation of the oxalic acid had occurred.

(4) No dark O_2 -sorption was observed on the $H_2C_2O_4$ -treated film, and no increase in the C_2H_4 dark uptake was apparent on any occasion.

Summary.

It may be concluded that the only part played by presorbed Na^+, Cl^- and OH^- is to reduce the olefin uptakes, presumably through a surface - blocking effect. Similarly, the presence of acids appears to suppress the photouptakes - particularly in the case of the hydrocarbons - without significantly affecting the dark sorptions. The only exception to the latter statement was in the case of the

dark C_3H_6 uptake which was considerably enhanced by pre-sorbed HCl gas. It is particularly noteworthy that the dark C_2H_4 sorption remained unaffected by any of the pre-treatments described in this section.

IV A. Experiments concerned with pre-illumination, and the effect of H_2O - treatment.

By the term "pre-illumination" is meant the illumination of a film in vacuo (i. e. with pumping) prior to the admission of a gas to the solid. Previous mention has been made of the parabolic growth of photocurrent under illumination (P. 23), and of the results obtained when O_2 is admitted to TiO_2 under conditions of steady-state illumination (P. 32). It seemed of interest to re-examine this effect, and to extend the investigations to the hydrocarbon-uptakes.

Tables 18 and 19 present adsorption and rate-data resulting from the admission of O_2, and C_2H_4 to films pre-illuminated for $18\frac{1}{2}$ hours. In both cases, the gas was admitted to the film with no break in illumination. When the corresponding reciprocal and log rate plots were constructed, it was found that:-

(a) In the case of O_2, parabolic kinetics held up to $q \simeq 46$ divs. ($t \simeq 120$ mins), and one Elovich line described the data from $q = 34$ ($t = 65$ mins.) onwards. A plot of q^2 vs t was linear up to ca. 130 mins.

(b) With C_2H_4, no parabolic section was evident. An excellently linear Elovich plot was obtained up to $t = 55$ mins., at which point another line branched off and fitted the remaining points well.

The extensive parabolic section observed in the O_2 uptake kinetics appears to substantiate the conclusion of McLintock (see P. 32) that this kinetic relationship is not determined merely by the rate of excitation of photo electrons from donor-levels. The absence of a parabolic section in the C_2H_4 uptake kinetics cannot be taken as significant, in view of the uncertain nature of these kinetics under normal conditions.

The behaviour of C_3H_6 could not be investigated under conditions of pre-illumination, owing to the dark adsorption.

It may be noted from Tables 18 and 19 that both uptakes were larger than normal. However, in the course of studying several C_2H_4 sorptions on pre-illuminated films, a particularly large variation in the amount and rate of uptake on different films was observed. The uptakes varied from being greater than normal (as in this example) to being negligibly small, and in such cases there appeared to be a rough correlation between loss of adsorptive activity, pumping time, and the efficiency of the vacuum maintained by the pumps. To illustrate this, a rough table may be drawn up of results chosen as being reasonably representative:-

Film	Approx. pumping time	Vacuum	$\Delta p_{(10)}$ (divs)
1.	65 hrs.	poor over later stages	23
2.	45 hrs.	poor	17
3.	24 hrs.	good	10
4.	50 hrs.	good	4
5.	48 hrs	good	4
6.	~ 8 days	pumping intermittent. Vac. good just prior to run	0.5

In all the above examples films of TiO_2(A) were pre-illuminated for periods not less than 12 hours. The Bourdon sensitivity was 0.024 mm div^{-1} (all the results in this section will be expressed at this sensitivity), and C_2H_4 pressures were ~ 50 mm. A "good" vacuum was one of 10^{-5} mm Hg. or better, and a "poor" one was ~ 10^{-2} mm Hg.

Although the relationship is by no means perfect, it seemed in general that the longer and more efficiently a film was evacuated under pre-illumination conditions, the smaller was the subsequent uptake of C_2H_4. (It should be stated at this point that on some occasions films were inadvertently exposed directly to the oil-pump, due to exhaustion of liquid N_2. The possibility does arise,

therefore, that contamination of the surface by vapours from the oil-pump could be, at least in part, responsible for the effects observed above. Nevertheless, the results given later in this section do suggest there to be a genuine deactivation effect associated with illumination.)

In view of the suggested dependence of uptake on pre-illumination and evacuation procedures, a series of experiments was carried out in order to investigate the possible relationships between surface water and oxygen-content, illumination and pumping time; and the influence of such factors on the photo-uptakes.

1. Effect of H_2O vapour.

Several experiments were carried out under both 'normal' and pre-illumination conditions, in which a photosorption was interrupted (by removing the gas, and in some cases discontinuing illumination), and the film left to stand for varying lengths of time in contact with small pressures of H_2O vapour. After pumping out the H_2O until no further desorption was detectable on the meter (ca. $\frac{1}{2}$ hour), the photo uptake was resumed and the rates of uptake immediately before and after the H_2O - treatment compared.

Examples of the result of such a procedure are given below.

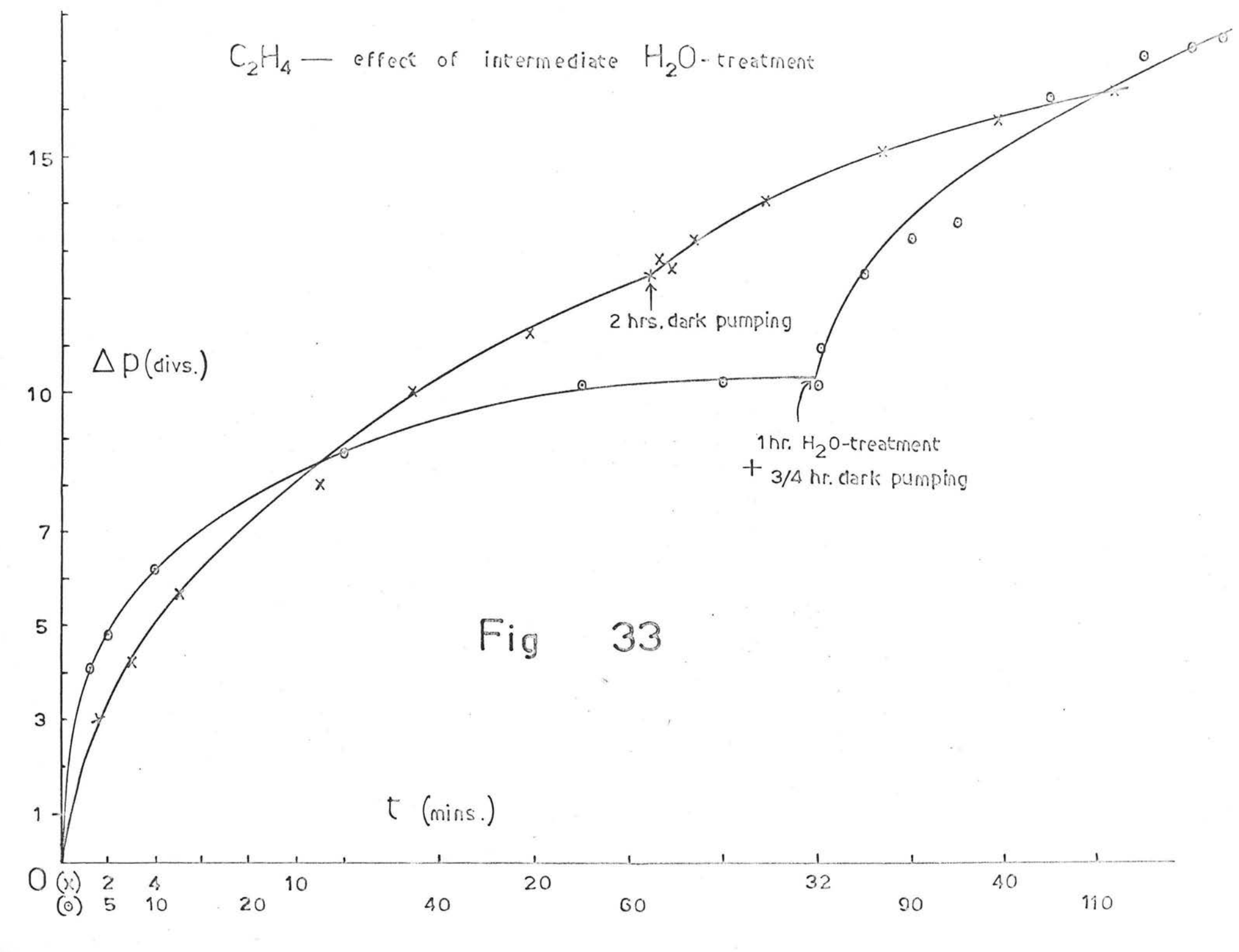

C_2H_4 — effect of intermediate H_2O-treatment
2 hrs. dark pumping
1 hr. H_2O-treatment
+ 3/4 hr. dark pumping
Δ p (divs.)
t (mins.)
15
10
7
5
3
1
0
(x) 2 4 10 20 32 40
(o) 5 10 20 40 60 90 110

Fig 33

Gas	Pre-treatment	Rate$_{(10)}$ prior to H_2O - treatment	Rate$_{(10)}$ following treatment
(1) O_2	-	0.15 div/min	0.32 div/min
(2) C_2H_4	Pre-illuminated	0.09 " "	0.31 " "
(3) C_2H_4	-	effectively 0 " "	0.35 " "
(4) C_3H_6*	-	0.14	0.32 " "

* these values refer to the photo-uptake of C_3H_6 - the dark uptakes before and after H_2O - treatment were, respectively, $\Delta p_{(25)}$ = 9.2 and 7.9.

As can be seen, there is a substantial increase in the rates following H_2O sorption in every case. It must be remembered here that interruptions in photo uptake have been shown (Sec. I) to give rise to rate-increases - at least with the olefins - in the absence of any H_2O - treatment. However, the interruptions in the present case were seldom for longer than ca. 1 hr., and it is considered that the observed rate-increases were generally greater than would be expected from this effect alone. In Fig. 33 the uptake curve for (3) above is shown plotted along with another C_2H_4 uptake which was discontinued for 2 hours, without H_2O - treatment.

C_2H_4 —— effect of pre-illumination in vacuo

(Table 20)

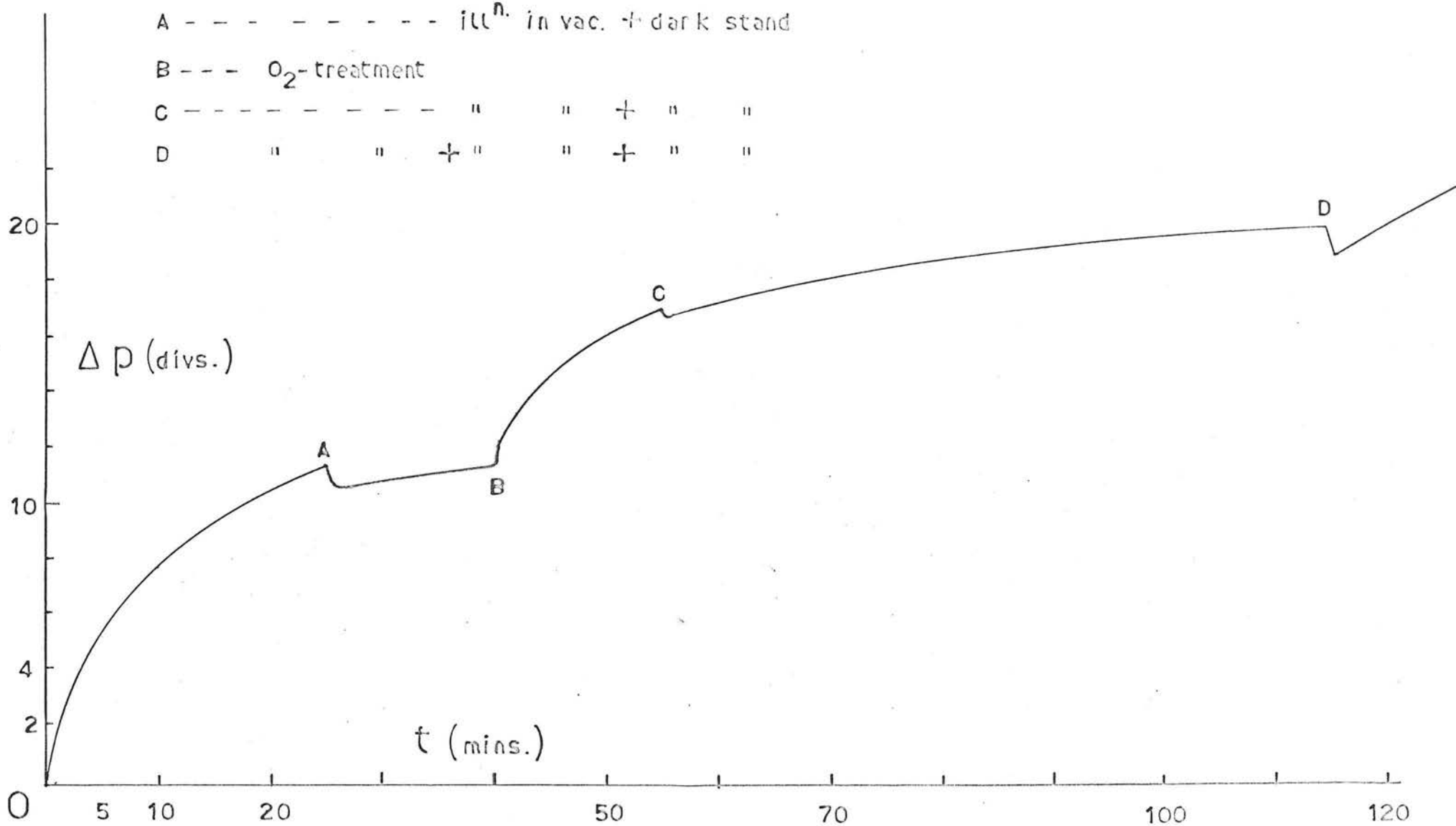


Fig 34

It was noticed that when a film was illuminated in vacuo for 19 hours and then pumped over the week-end in the dark, there was virtually no uptake of C_2H_4 over 15 mins., when the gas was admitted to the reaction vessel and the film re-illuminated. This seemed to support the idea that illumination combined with exhaustive pumping deactivates the surface. Moreover, it seemed that a dark stand following the pre-illumination did not reactivate the TiO_2.

However, it was first necessary to show that the deactivation was, at least in part, associated with illumination, and not due entirely to exhaustive pumping. Accordingly, a film of TiO_2(A) was held under high vacuum ($\sim 10^{-5}$ mm) for ca. 30 hrs., 50 mm C_2H_4 was admitted, and the film illuminated. There was a moderate uptake of gas ($\Delta p_{10} = 7.6$), and, after 25 mins. ($\Delta p = 11.3$) the C_2H_4 was pumped out. The film was then illuminated, with pumping, overnight, the light turned off for 1 hr., more C_2H_4 admitted and the film re-illuminated. A drastic fall in rate was observed - i. e.

Rate over last 10 mins. prior to overnight illumination = 0.21 div./min.

" " first " " following overnight illumination = effectively 0

(Fig. 34 Pt. A, Table 20).

C_2H_4 — effect of intermediate evacuation, illumination in vacuo, and dark O_2 treatment

(Table 21)

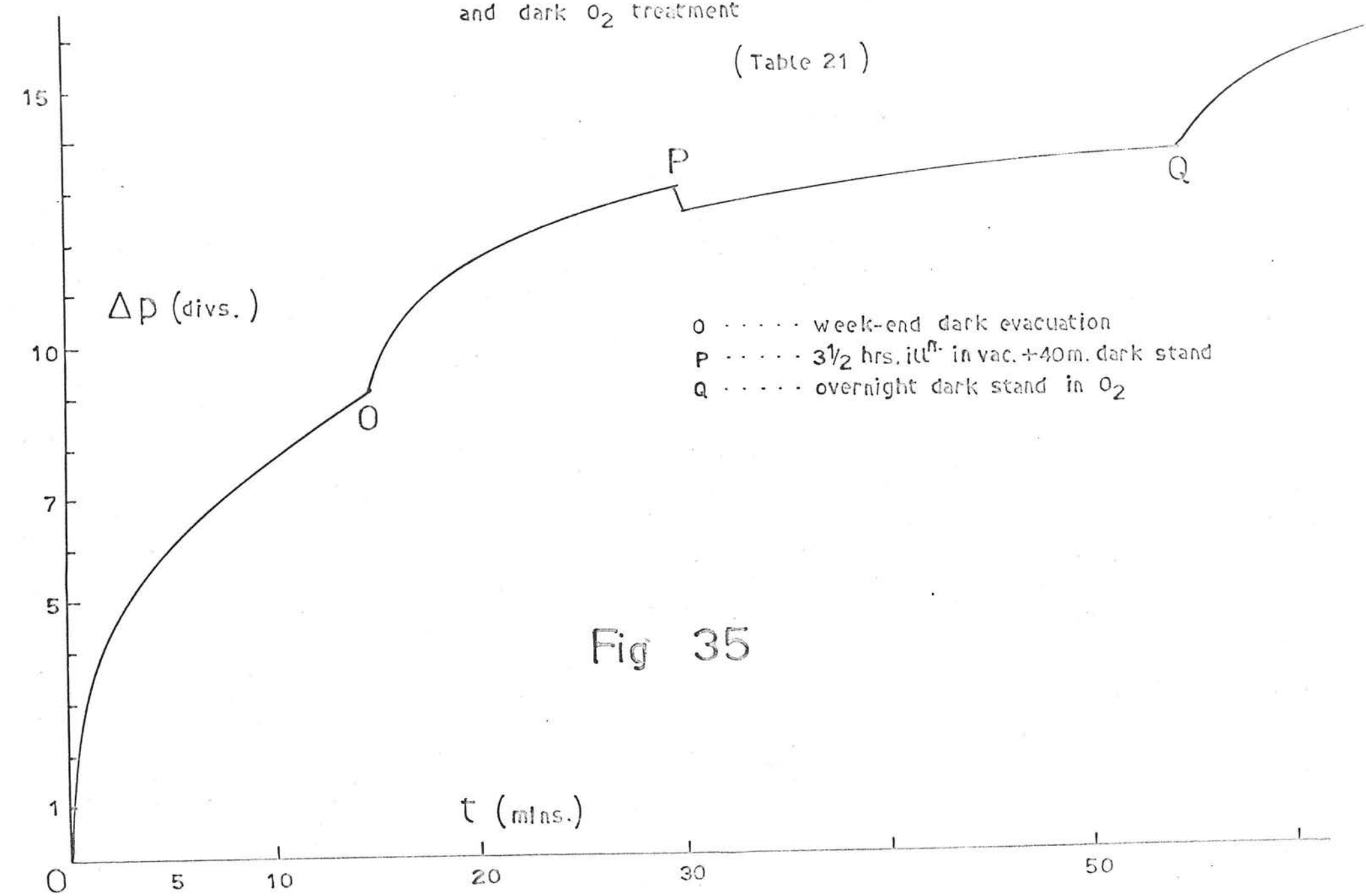


Fig 35

This effect, when examined on a number of films, was perfectly reproducible, and, since an overnight evacuation in the dark gives rise, if anything, to an increase in activity, it may be taken that there is a significant difference when the evacuation is accompanied by illumination. Both effects are shown in Fig. 35 (Table 21), where a week-end evacuation of a C_2H_4 - treated film resulted in an increased activity. After $3\frac{1}{2}$ hrs. illumination followed by a 40 min. dark period, however, the rate fell from 0.14 to approx. 0.05 div./min.

It was shown (19) that when a film was pumped in the dark following an illumination in vacuo, considerably more H_2O was liberated than would normally be the case. It was, therefore, of interest to investigate the effect of H_2O - treatment on films deactivated to C_2H_4 in the above manner.

In the original case, where there was zero uptake over 15 mins., treatment with 8 mms. H_2O for 15 mins. resulted in a subsequent C_2H_4 photo uptake of 3.2 divs. over 20 mins. After an overnight stand in the dark, re-illumination gave rise to a further pressure-decrease of ca. 1 div. in 15 mins., by which time the rate was effectively zero. H_2O - treatment for 3 hrs. then resulted in a further, steady pressure-decrease (2.2 divs. in 15 mins.). Although the rates were all low, it is of significance that there

was a final uptake of 11 divs. (in 130 mins.) whereas, before the H_2O treatment, virtually no uptake was observed.

The same deactivation effects were encountered with C_3H_6 photo uptakes, e. g.

Rate of photo uptake over last 10 mins. prior to overnight illumination = 0. 28 divs. $min.^{-1}$

" " " over first 10 mins. following overnight illumination = 0

though the dark uptake was in this example found to be increased (Δp_{25} = 11. 5 divs)

With O_2, however, a slight increase in the rate was observed following the overnight illumination.

e. g. A "normal" sorption was carried out for 7 mins. (Δp = 9. 8), when the gas was pumped out and the film illuminated in vacuo overnight. After a dark stand of $1\frac{1}{2}$ hrs., O_2 was readmitted and the photo uptake resumed:-

Rate over last 3 mins. prior to overnight illumination = 1. 0 div. min^{-1}

" " first " " following " " = 1. 3 " "

Similarly, when a C_2H_4 - treated film was pre-illuminated in the same way, the subsequent O_2 uptake was, if anything, more rapid than expected for the non-preilluminated case.

2. Effect of O_2 - treatment.

Even in the case of almost complete destruction of activity

towards C_2H_4, the admission of small amounts (ca. 5 mms.) of O_2 to the C_2H_4 gas phase resulted in rapid, large pressure-decreases, these being greater than expected for pure O_2 uptakes. Presumably the initial traces of O_2 taken up reactivated the surface.

A film which had been deactivated to C_2H_4 by pre-illumination, followed by a dark stand, was illuminated in 1.5 mm O_2 for 125 mins., by which time 47 divs. had been taken up, and adsorption had virtually ceased. After pumping for 45 mins. in the dark, C_2H_4 was readmitted and the film re-illuminated. The rate of uptake prior to O_2 - photosorption was O, and in the first 10 mins. after the O_2 - treatment, was 0.47 div. min.$^{-1}$ (Fig. 34, pt. B). The illumination was then discontinued for 40 mins. while the C_2H_4 was pumped out, and the film re-illuminated overnight. After a dark period of 1 hour, the C_2H_4 photo uptake was resumed (Pt. C):-

Rate prior to overnight illumination = 0.25 div. min.$^{-1}$
" after " " = 0.06 " "

i.e. again, a loss of activity.

It seemed possible, in the light of McLintock's (4) photo conductivity experiments (see P. 25), that a prolonged photo uptake of O_2 might be "irreversible" in the sense that illumination in vacuo would not then affect the activity of the film towards

C_2H_4 sorption. Accordingly, the same film was illuminated in 50 mms O_2 for 4 hrs., and the O_2 then pumped out with no break in illumination. After the usual overnight illumination and 1 hour dark period, the C_2H_4 photo uptake was resumed. The result is shown in Fig. 34, pt. D. If the initial, immediate pressure-increase is ignored, the rate over the first 10 mins. is approx. 0.2 div/min, which follows on, roughly, from pt. C. The observed rate is not, however, as great as would be expected on a film freshly treated with O_2 - i.e. non-preilluminated. Thus it seemed that, despite the prolonged treatment, the adsorbed oxygen was still modified to some extent by illumination - at least with respect to a subsequent C_2H_4 uptake.

One final result of significance in this section can be seen from Fig. 35, pt. Q. It would seem that a stand in contact with 10 mm O_2 in the dark reactivated this film to some extent. It is extremely unlikely that such a stand in contact with C_2H_4 would give rise to a similar result.

In summary, it may be said that :-

(a) Prolonged and efficient evacuation combined with illumination deactivated TiO_2 (A) films towards C_2H_4 and C_3H_6 photo adsorption. This was particularly true when the illumination was succeeded by a dark period of ca. 1 hour. In contrast, the tendency with O_2 was

towards increasing the rates of uptake.

(b) Treatment of both active and inactive films with H_2O vapour resulted in increased rates of photo uptake of all three gases.

(c) Photo uptake of O_2 on films deactivated to C_2H_4 resulted in large increases in subsequent C_2H_4 uptakes. Pre-illumination in vacuo, however, of such O_2 -treated films resulted again in partial loss of activity. Conversely, photo uptake of C_2H_4 increased the rate of a subsequent O_2 uptake, but illumination in vacuo did nothing to alter this result.

(d) Treatment of a film inactive to C_2H_4 with O_2 in the dark resulted in a partial recovery of activity.

(e) The kinetics of O_2 and C_2H_4 uptake were unaltered by pre-illumination.

IV B Hydrocarbon uptakes on NH_3 - treated TiO_2

It has been shown (3) that a dark sorption of NH_3 takes place on TiO_2, resulting in an equimolar displacement of H_2O from the surface. A succession of alternate NH_3 - treatments and evacuations should, therefore, reduce considerably the surface concentration of adsorbed H_2O. Thus, in view of the possible dependence of hydrocarbon uptake on surface water suggested by the results of Sec IV A, it was considered of value to perform a set of

experiments similar to those of Sec. IV A, on films which had been pretreated with NH_3.

The results of this section will be expressed in units of divisions, sensitivity 0.050(3) mm. div.$^{-1}$, in order to facilitate comparison with the results obtained on untreated TiO_2.

Due to excessive adsorption within the cell, it was found necessary to leave the NH_3 in contact with the latter for several hours before admitting the gas to the reaction-vessel. The sorption on TiO_2 (A) was found to be very rapid initially, but dying off fairly quickly - e. g. with NH_3 - pressure = 23 mm.

rate over first $\frac{1}{4}$ min. = 86 divs/min.

but " between 73 and 75 mins. = 0.5 div. /min.

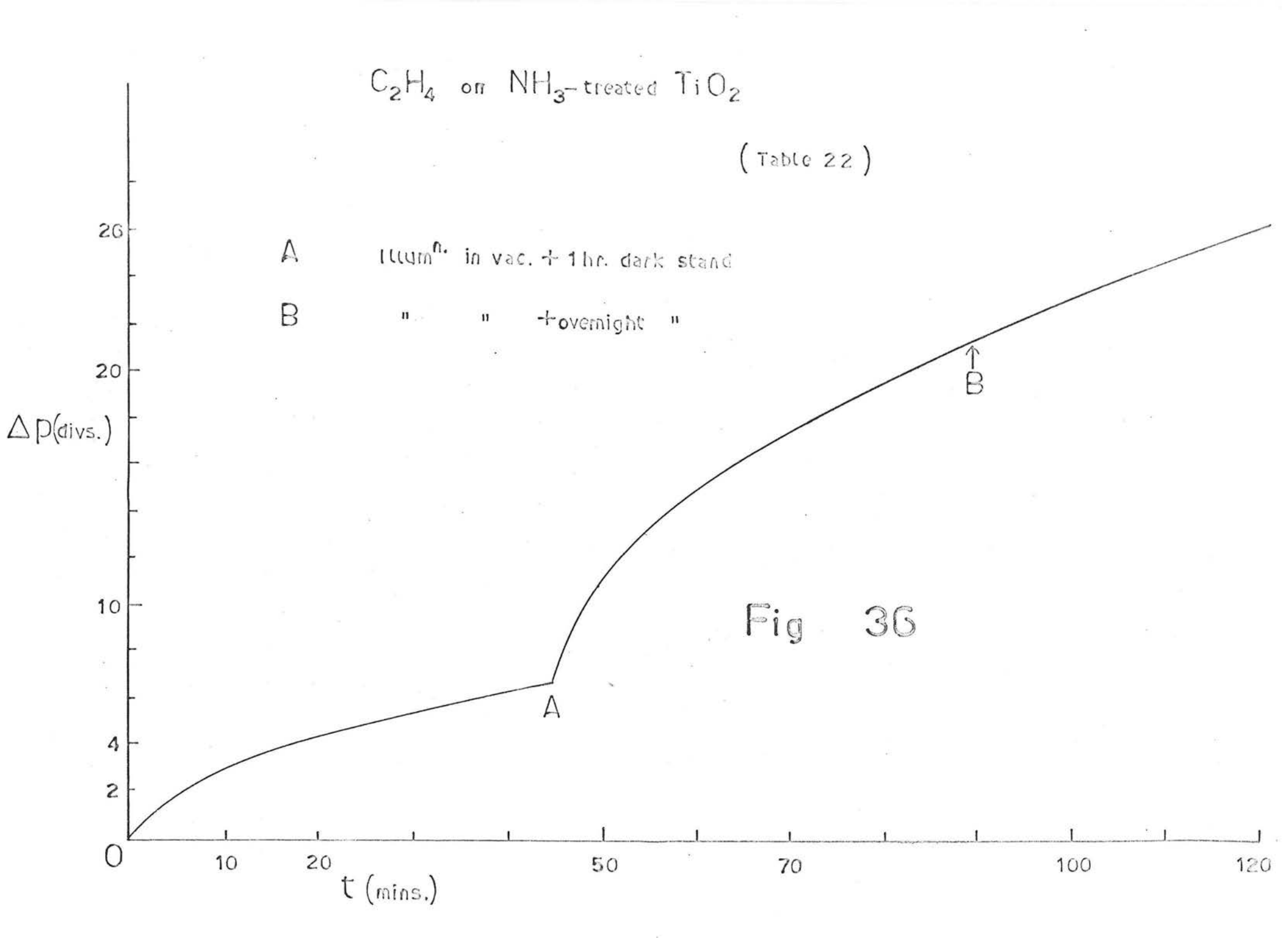
The <u>dark</u> uptakes of C_2H_4 and C_3H_6 were not found to be significantly altered by the pre-sorption of NH_3 -

e. g. for C_3H_6 before NH_3 treatment $\Delta p_{10} = 5.6$, $\Delta p_{30} = 6.7$

and after " " $\Delta p_{11} = 4.9$, $\Delta p_{30} = 6.7$

The photo-uptake of C_2H_4 was, however, found to be lowered slightly - e. g. in one experiment a film was treated with ca. 20 mms. NH_3 for ~4 hrs. and then pumped overnight. The subsequent uptake of C_2H_4 was $\Delta p_{10} = 2.8$, $\Delta p_{45} = 6.7$ divs.

The effect of <u>intermediate</u> NH_3 - treatment (i. e. using a procedure similar to the intermediate H_2O - treatment of Sec. IV A) on both C_2H_4 and C_3H_6 <u>photo</u>sorptions is illustrated below:-


C_2H_4 on NH_3-treated TiO_2
(Table 22)
A Illumⁿ. in vac. + 1 hr. dark stand
B " " + overnight "
Δ p(divs.)
t (mins.)
0
2
4
10
20
20
10
20
50
70
100
120
A
B
Fig 36

Gas	(n)	Rate over last 'n' mins. before NH_3-treatment (divs. $min.^{-1}$)	Rate over 1st 'n' mins. after NH_3-treatment (divs. $min.^{-1}$)
C_2H_4	(10)	0.14	0.14
C_2H_4*	(5)	0.19	0.32
C_3H_6	(10)	0.10	0.09
C_3H_6	(5)	0.18	0.12

* In this example, the film was given only 1 hr's preliminary pumping, but 5 hrs' pumping following an overnight stand in 29 mins. NH_3, and it is probable that the rate-increase is due to this pumping, after the usual behaviour of untreated films. This is supported by the fact that a subsequent overnight stand in vacuo followed by $2\frac{1}{2}$ hrs' pumping gave rates (over 5 mins.) before and after this treatment of 0.06 and 0.21 div./min. respectively.

Thus it seemed in general that intermediate NH_3-sorption lowered the rates of photo uptake, though the effect was not pronounced.

A more striking result is illustrated in Fig. 36 (Table 22), which shows the effect on a C_2H_4 uptake of <u>illumination in vacuo</u> of a NH_3-treated film. The film had been pre-treated with NH_3, and pumped overnight. At point 'A' the film was illuminated in vacuo

overnight, then pumped for 1 hr. in the dark. At 'B' the film was evacuated with no interruption in illumination for $4\frac{1}{2}$ hrs., and then pumped overnight in the dark. The rates over 10 mins. before and after 'A' were, respectively, 0.09 and 0.63 div./min. : and over 5 mins. before and after 'B' were 0.17 and 0.17 divs. $min.^{-1}$ A similar effect was observed on a second film, where the rates (over 5 mins.) before and after illumination in vacuo overnight, followed by 1 hr's dark pumping, were 0.06 and 0.11 div./min., if a small thermal pressure-increase following the period of illumination is ignored.

It thus seemed that the effect of pre-illumination in vacuo of NH_3 -treated films was <u>not</u> to lower the subsequent rates of C_2H_4 photo uptake, as found on untreated films; rather was an <u>increase</u> in rate observed.

<u>NH_3/hydrocarbon mixtures.</u>

Following two C_3H_6 photo uptakes with an intermediate NH_3 - treatment, 12.5 mms NH_3 were admitted to an evacuated film, and the sorption allowed to go to completion overnight. C_3H_6 was then admitted to the cell, and any pressure-changes again allowed to go to completion, before the two gases were mixed in the reaction-vessel. The partial pressures were then 8.5 mm NH_3 : 29.0 mm C_3H_6. A dark pressure-<u>increase</u> was observed, of 8.3 divs. in 25 mins. After ca. 115 mins., no Δ p's were evident, and illumination then

led to a further, very slight pressure-increase (0.2 div. in 15 mins). On putting off the light, a pressure-decrease of 1.9 divs in 15 mins. was observed.

A similar effect was observed with C_2H_4, though the pressure-changes were here much smaller. An initial pressure-increase of 3.5 divs. in 70 mins. reverted to a very slow decrease after ca. 80 mins. illumination, the total observed decrease being only 1.5 divs in 80 mins.

One interpretation of the above results might be in terms of a dark displacement of more than one NH_3 molecule by the sorption of one of the bulkier hydrocarbon molecules. In the case of C_3H_6, the observed pressure-increase was of roughly the same order of magnitude as the usual dark uptake, indicating a 2 : 1 displacement. With C_2H_4, however, the pressure-increase was much greater than the dark sorptions normally detected on untreated films.

Obviously, the photo uptakes have either been completely suppressed, or are proceeding accompanied by the same displacement.

The kinetics of photo uptake were found to be unaltered by pre-sorbed NH_3.

V. Uptake of C_2H_4 and O_2 on NO - treated TiO_2 (B)

In the light of the evidence presented in the Introduction (P. 9) for the existence of a high concentration of paramagnetic centres in the surface of TiO_2, it seemed possible that the sites responsible for C_2H_4 photoadsorption might behave like free radicals. Nitric oxide is a gas noted for its reactivity towards free radicals, and it thus might be expected that pre-sorption of NO would poison the surface towards C_2H_4 uptake. This effect has been observed for C_2H_4 uptake on γ - irradiated SiO_2 (83).

NO - sorption

This uptake has previously been studied by Kennedy (2) and MacLean (3, 14). It was found that the photoadsorption of the gas was accompanied by the production of N_2O in the pressure-ratio 1:4 i.e. the pressure-decrease was represented by

$$4NO_{(g)} \longrightarrow N_2O_3(ads.) + N_2O_{(g)} \qquad (1)$$

This equation was revised by MacLean who found evidence for surface nitrite, and that more N_2O was produced by degassing.

i.e. $$3NO \longrightarrow NO^-_2 + N_2O \qquad (2)$$

In the present investigations NO was found to be taken up by TiO_2(B) films in the dark, only in small amounts ($\sim$0.7 - 1.7 divs.; sensitivity 0.050(3) mm./div.). The photoadsorption, however,

was found to be very rapid and extensive.

e. g. at NO-pressure = 33. 0 mm.

$\Delta p_{(5)}$ = 15. 1 divs., $\Delta p_{(100)}$ = 101. 4 divs.,

at sensitivity 0. 050 mm/div. (see Table 23).

The kinetics of photo-uptake were found to be similar to those for O_2 e. g. in the above example, the parabolic law held up to Δp = 70 divs., t = 50 mins., or alternatively two Elovich lines could be fitted into the data, the break occurring at Δp = 29, t = 12. 5 mins. It must be remembered that, on the basis of equation (1) above, a pressure decrease of 'x' divs. corresponds to an uptake of NO of $4x/3$ divs. Further, from equation (2), this corresponds to the production of $4x/9$ divs. NO_2^- on the surface. Wherever 'Δp' values appear in the following tables, they refer to the observed pressure-decreases, and not to the actual uptake of NO.

The reversibility of the NO sorption was examined only on one film previously treated with photoadsorbed O_2. The rates of pressure-decrease over 15 mins. before and after a week-end stand in vacuo plus 1 hr. 's pumping, were, respectively 0. 61 and 0. 78 div. $min.^{-1}$ --- i. e., like the C_2H_4 uptakes, intermediate evacuation had caused an appreciable increase in rate.

C_2H_4 on NO-treated films.

The table below shows the observed photo-uptake of C_2H_4 at t = 30 and t = 60 mins. on two films pre-treated with different amounts of NO, along with an uptake observed on untreated TiO_2(B) under the same pumping conditions (~21 hrs. with the rotary pump only). All results in this section are expressed at sensitivity 0.050(3) mm/div.

Δp observed in NO (divs.)	$C_2H_4q(30)$ (divs.)	$C_2H_4q(60)$(divs.)
-	6.7	9.0
26.5	4.3	7.0
101.4	1.6	3.0

As can be seen, presorbed NO decreased the C_2H_4 uptakes, the extent of the decrease depending on the amount of NO taken up. This is not the behaviour expected on the basis of C_2H_4 sorption proceeding via a free-radical mechanism, where trace amounts of NO should suffice to inhibit the reaction. It appeared more likely that the NO was simply blocking regions of the surface normally acting as photoadsorption sites for C_2H_4. The results were, nevertheless, of interest since the implication was that at least some of the photo-sites were common to NO and C_2H_4. Similarly, it was found by Kennedy (2) that the O_2 and

NO uptakes mutually interfered. It therefore seemed possible that the photosorptions of O_2, NO and C_2H_4 were intimately interrelated, and that a quantitative survey of the effect of pre-sorption of these gases on the uptake of the others, might provide information on the nature of the surface-sites involved.

(1) O_2-uptakes

Pre-treatment		Uptake after 'n' mins. Δp_n (divs.)		
(1)	(2)	$\Delta p(5)$	$\Delta p(10)$	$\Delta p(60)$
-	-	2.8	4.1	11.5
-	-	3.1	4.6	11.6
NO (Δp=75.8divs.)*		2.3	3.8	14.1
NO (1210 mins. illumination)‡		1.1	1.9	7.0
C_2H_4(12divs)	NO(Δp=101.3)	1.8	3.2	13.9

(2) NO-uptakes

Pre-treatment	$\Delta p(5)$	$\Delta p(10)$	$\Delta p(60)$
-	15.1	24.9	77.1
-	15.2	25.0	75.8
-	14.2	22.9	69.5
O_2 (16.0 divs.)	14.7	24.8	77.8
O_2 (1200 mins. illumination)	10.4	18.1	58.9
C_2H_4 (12.0 divs.)	13.1	22.1	68.9
C_2H_4 (51.8 divs.)	10.3	17.8	58.7

(3) C_2H_4-uptakes

Pre-treatment (1)	(2)	(3)	$\Delta p(10)$	$\Delta p(60)$
-	-	-	4.5	9.0
-	-	-	6.2	10.7
O_2(11.5 divs.)	-	-	10.2	17.5
NO (Δp=101.4)	-	-	0.6	3.0
NO (Δp=26.5)	-	-	1.9	7.0 **
NO (Δp=75.8)	O_2(14.1)	-	2.7	6.6
NO (1210 mins. illumination)	O_2(7.4)	-	0.7	2.1
O_2 (16.0)	NO(Δp=77.8)	-	1.2	4.3
O_2(1200 mins. illum^n)	NO(Δp=79.6)	-	0.5	3.2
C_2H_4 (9.0)	NO(Δp=101.3)	O_2(13.9)	2.3	5.5
C_2H_4(51.8)	NO(Δp=58.7)	Overnight pre-illum^n + 1 hr. dark stand.	1.2	Δp_{20}=2.1

Notes.

(a) Although the dark C_2H_4 sorptions were unaffected by pre-sorption of NO, a small dark uptake of O_2 was observed on films freshly treated with NO - i. e. in the two examples marked * and ≠ in table (1). These uptakes were 0. 8 in 25 mins. and 0. 4 div. in 15 mins. respectively.

(b) Kennedy (2) made the observation that pre-sorption of NO decreased subsequent rates of O_2 uptake. Although this was verified for the early stages of adsorption, the eventual uptake was sometimes greater than normal - e. g. in example * in table (1).

(c) The kinetics of O_2 uptake * on a NO-treated film could be described by a parabolic expression over 60 mins., or alternatively by one Elovich line after t = 2. 5 mins. More surprisingly, it was found that the data of C_2H_4 sorption ** could similarly be best represented by a parabolic expression over 60 mins., though the points were badly scattered. An Elovich line also fitted the data from 9 mins. onwards.

VI The Hydrocarbon Oxidations.

The photooxidations resulting from illumination of TiO_2 in C_2H_4/O_2 and C_3H_6/O_2 atmospheres have been studied previously (4, 15). The experiments described in this section were aimed at verifying the stoichiometry of the oxidations, but must be considered to be of a preliminary nature, since time did not permit their completion.

(1) Oxidation of C_2H_4

Illumination of C_2H_4/O_2 mixtures over TiO_2 gave rise to large, rapid pressure-decreases. Subsequent pumping of the film through a cold-trap, and analysis of the mixture so obtained by vapour-pressure measurements, showed the presence of CO_2 and H_2O as well as residual C_2H_4. Quantitatively, conflicting results were obtained at small partial pressures of C_2H_4 and O_2, presumably due to inaccuracies in pressure-measurements, and retention of products by the solid. Measurements with larger partial pressures, and longer times of illumination, however, produced concordant results. A typical experiment is described below.

50 mms. C_2H_4 + 126 mms. O_2 were illuminated over 0.100g. TiO_2(A) for 10,010 mins. The "reaction-volume" here

included the whole lower line + cell + Bourdon gauge, and the reaction-vessel side-arm was charged with P_2O_5. After ceasing illumination, the total pressure in this volume had fallen by 17.5 mm. to 158.5 mm. The trap was then surrounded by liquid N_2, and after ca. 1 hr. the pressure had fallen to 120 mm. The gases were pumped slowly through the cold-trap for ca. 2 hrs., the vapours re-expanded to a total pressure of 78.5 mm., and vapour-pressure measurements were then made on the manometer, in the manner described on Pp. 56-57. The results are shown plotted in Fig. 11. The analysis mixture was found to consist of 25.0 mms. C_2H_4 + 50.0 mms. CO_2, + 3.5 mms. residual gas, presumably H_2O-vapour. i.e. in the photo-reaction, 25 mm. C_2H_4 had been consumed, and 50 mm. CO_2 produced. Thus, purely on the basis of the $CO_2 : C_2H_4$ ratio, the results fitted perfectly the stoichiometric equation proposed earlier (4):-

$$C_2H_4 + 3\,O_2 = 2\,CO_2 + 2\,H_2O$$

The H_2O produced will have been largely absorbed by the P_2O_5, but the situation regarding O_2 is not so clear. The results suggest that only 6 mms. (126 - 120) O_2 had been consumed, which is completely incompatible with the above equation. Possibly either (a) all the condensible vapours had not condensed

after the 1 hr. stand in contact with the cold-trap, or (b) a leak of air had occurred into the pressure-measurement system during illumination, or (c) some other 'permanent' gas was present, e. g. CO, arising from partial oxidation. These alternatives were not resolved owing to lack of time.

(2) Oxidation of C_3H_6

Analysis of the products of C_3H_6 oxidation was complicated by two effects. First, it was found that C_3H_6/CO_2 mixtures, in the presence of an excess of O_2, did not wholly condense at liquid N_2 temperature; and secondly, these mixtures were not resolvable by vapour-pressure analysis (e. g. see Fig. 12). The first of these difficulties is illustrated by the following experiment:-

After illuminating 51. 5 mm C_3H_6 : 81. 5 mm. O_2 over TiO_2 (B) for 4275 mins, the total pressure had fallen to 117 mms. A $1\frac{1}{2}$ hr. stand in contact with a trap surrounded by liq. N_2 resulted in a further pressure decrease to 80. 4 mm. However, this pressure was found to be peculiarly dependent on the liq. N_2-level - topping up the level resulted in a pressure-decrease, followed by an increase as the N_2 evaporated. These fluctuations were too great to be due entirely to expansion and contraction of the per-

manent gas, and incomplete condensation of the condensible gases was indicated. The lowest pressure recorded at this stage was 76.0 mm.

After overnight pumping through the cold-trap, the condensed material was found by vapour-pressure analysis to consist of 61.4 mm(CO_2 + residual C_3H_6), and 2.6 mm. of a gas with vapour-pressure corresponding roughly with that of H_2O.

At this point it may be said that, by mathematical manipulation, it was immediately possible to deduce the difference between CO_2 produced and C_3H_6 consumed, since:-

if C_3H_6(initial) = P_1 and $CO_2 + C_3H_6$(residual) = P_2

then C_3H_6(consumed) = C_3H_6(init.) - C_3H_6(resid.)

$$= P_1 - P_2 + CO_2$$

$$\therefore CO_2\text{-}C_3H_6\text{(consumed)} = P_2 - P_1$$

This difference was here 61.4 - 51.5 = 9.9 mm.

An attempt was made at separating the C_3H_6 from the CO_2 by absorbing the latter with NaOH pellets. This method had previously been used successfully to separate small amounts of CO_2 and N_2O (17). The absorption was, however, found to proceed extremely slowly (~2 mm/day.) and was not complete after 7 days. The experiment was, therefore, abandoned at this point.

Further experiments were conducted in which use was made of gas-chromatography (see P. 59) in order to estimate (a) the CO_2 : C_3H_6 ratio only, and (b) the relative amounts of C_3H_6, CO_2 and O_2 present in the gas-phase following the photo-reaction. In (b) a small sample of the gas-phase not condensed by 'Cardice'/acetone was measured out using the Bourdon gauge, and passed through the column in the normal way. By substracting the sum of C_3H_6 + CO_2 indicated by the chromatograph from the total pressure, it was hoped to make an estimate of the proportion of O_2 originally present. The results of two experiments are shown below:-

(a) Initial partial pressures = 54.1 mm. C_3H_6 : 102.2 mm. O_2

Illumination time = 4220 mins.

Vapour-pressure analysis:- $CO_2 + C_3H_6 = 56.4$ mm.

(CO_2 - C_3H_6 used = 2.3mm)

H_2O and/or HCHO = ca. 1 mm.

Chromatography results

C_3H_6 used (mm.)	CO_2 produced (mm.)	CO_2/C_3H_6 used
26.2	28.5	1.09
27.1	29.4	1.09
28.3	30.6	1.08

(Estimate of O_2 used from liquid N_2 - condensation = O).

(b) Initial partial pressures = 20.7 mm. C_3H_6: 88.4 mm. O_2

Illumination time = 4065 mins.

Chromatography results

Residual O_2 (mm.)	Residual C_3H_6 (mm.)	CO_2 produced (mm.)
67.9	24.0	10.4
87.4	6.5	8.3

The very large variation in the results of (b) makes them uninterpretable. The difficulty here may have been associated with the sampling procedure outlined above. Properly representative samples were obviously not obtained, possibly due to the different mobilities of the three gases.

However, the results of (a) were much more consistent, and were verified by another experiment carried out under similar conditions, where again the ratio $CO_2 : C_3H_6$ used was 1 : 1 (range 1.07-1.13).

The stoichiometric equation proposed by McLintock (4), i.e.

$$C_3H_6 + {}^5/_2\, O_2 = CO_2 + 2\ HCHO + H_2O$$

may thus be said to have been verified only with respect to the $CO_2 : C_3H_6$ ratio. The very small amounts of H_2O and/or HCHO recovered (~1-4 mms.) may be explained by retention by the solid. No evidence was, however, obtained for the presence of formal-

dehyde on the evacuated surface following photo-reaction, using the spot-test outlined on P. 59.

Part 4

DISCUSSION

DISCUSSION

In this section an attempt will be made at explaining the uptakes of oxygen, hydrocarbon and nitric oxide in terms of surface sites and the band-structure of the solid. Features of the uptakes that must be examined are the kinetics, the observed behaviour in the presence of various adsorbates, and after pre-illumination, and any other observations described in Part 3. In such an attempt, attention will be paid to the previously obtained results presented in Part I - particularly those concerned with surface and conductivity effects, and spectroscopic observations. The various reaction schemes outlined in 1. will be discussed critically in the light of the present results and ideas.

I. The O_2 Uptake.

Attention was focussed, in Part 3, principally on the olefin-sorptions. However, it is of value to consider what new knowledge has been gained of the O_2-sorption, and to review briefly previous proposals as to its nature. Although it is not in fact, possible to treat the uptakes of O_2, olefin and NO in isolation from one another, in view of their suggested inter-dependence, the topics dealt with here will be concerned with O_2-sorption on an "untreated" titania surface, and a discussion of features relevant to all the uptakes

(e. g. the active sites) will be postponed until later.

Perhaps the most significant aspect of the oxygen photo sorption apart from the kinetics, is the observation (3, 19) that it is attended by the production of H_2O. Some connection may be sought between this result and others concerned with the hydrated surface, photo-conductivity and pre-illumination.

The original interpretation (3) of this process was in terms of Lewis acid - type sites, and the action of light was supposed to cause a reaction such as

$$TiO_2,\ H_2O \longrightarrow H^+ + \epsilon + TiO_2.\ OH \ldots\ldots \quad (1)$$

Four such sites were then thought to be utilised by one O_2 molecule, to produce two H_2O molecules. (See P. 34). Many objections may be raised to this scheme. For instance, no explanation is forthcoming of the kinetics or photo-conductivity results, and it has been shown (4, 15) that O_2 is photoadsorbed on "dry" films, and is accompanied by the production of only negligible amounts of H_2O.

The scheme was, however, later modified by McLean and Ritchie (14) in order to bring it in line with the concept of 'A' and 'B' sites first proposed by Kennedy et al (13). In this modified version, O_2 is thought to be taken up initially reversibly, probably as O^-_2, and interaction of this species with the Lewis-sites is considered to correspond to Kennedy's irreversible uptake on

the B-sites. It is interesting to note the similarity between this concept and the ideas of McLintock (4) and Bews (17), in both of whose schemes the initial adsorption is as a reactive entity capable of oxidising sorbed hydrocarbon, or carbohydrate. The possibility of the Lewis sites representing "oxidisable entities" in the terminology of Bews, has already been mentioned (Introduction). Some of the previous objections to the validity of equation (1) are removed by the above modification - e. g. the authors propose that water is produced by the photo reaction in a maximum molar ratio of 2 H_2O : 1 O_2 sorbed, and that such H_2O may be retained by abnormally dry films to some extent.

Basically, the objections that remain are based on results concerned with pre-illumination, and with water-extraction experiments carried out by Vickerman (19) in this Department. The latter experiments were aimed at examining the H_2O-content of the films, using Karl-Fischer titration techniques. Films were extracted with anhydrous methanol following O_2 photosorption, and were found to carry a higher water-content than films untreated with O_2. It seemed likely that H_2O lodged in a hydroxyl-vacancy, as in equation (1), would be capable of extraction in this way, and therefore on the basis of (1) a decrease in surface H_2O -content might be expected, since O_2 sorption is supposed to give rise to

$$4\ TiO_2,\ H_2O \xrightarrow{O_2} 2\ H_2O + 4\ TiO_2,\ OH$$

A second observation in the same vein, which has already been noted (3 (IV A))was that when a film was pumped through a cold-trap in the dark, following a period of illumination in vacuo, much more water was collected than was normally evolved in the absence of illumination, though this quantity was not so great as that produced during O_2 -sorption. Strangely, the same was not true when a film was evacuated during illumination, only slightly more H_2O being evolved than normal during both illumination, and the following dark period. It is interesting to note in this connection that Kennedy (2) has made the observation that illumination of his samples in vacuo resulted in the liberation of small amounts of a gas not condensed by liquid O_2. This process was stated to be accompanied by the creation of active sites responsible for the dark uptake of O_2 and NO. This observation has never since been verified, however, and in the present studies no photo-desorption was ever detected on the proximity meter over several hours' illumination in vacuo.

In any event, it is difficult to see how the above facts are to be explained on the basis of equation (1). Even if it were possible to account for the H_2O liberated following illumination in vacuo, the removal of H_2O situated on Lewis sites would be

expected to result in a lowering of subsequent O_2-uptakes; whereas the present researches indicate a small increase in uptake (3 (IV A).)

Kinetics of O_2-uptake.

Reaction-schemes devised in order to explain the observed kinetics have been outlined in Part I. In most cases, the conclusion arrived at was that the truly characteristic kinetics were described by an exponential expression (e. g. the Elovich equation), and that the initial process, which normally differed kinetically from the later stages, somehow represented the uptake under non-equilibrium conditions. For example, the parabolic expression was associated by McLintock with electronic equilibration, and by Bews with oxidation of surface impurities. This expression, which may be written,

$$(q + qo)^2 = kt + qo^2$$

had previously been interpreted in terms of surface migration, and this same explanation has been invoked to account for other kinetic expressions - e. g. the $q^{3/2}$ relation observed with some C_2H_4 uptakes (77). It is worth-while, therefore, to consider this possibility in more detail.

First, it should be said that there is no direct evidence for such a migration. However, calculations based on the assumption that rates of migration are initially rate-determining, are stated by Kennedy to give rise to parabolic kinetics, if the process is

treated as analogous to the diffusion of oxide ions in thin metal-oxide layers. In contrast, however, Smith and Metzner (85) report adherence to an equation of the type

$$I_A = \text{const. } xp \frac{\partial x}{\partial p} + \text{const.}^{1}. \quad x^{2},$$

for the rates of migration of several physisorbed gases on Al_2O_3, at constant temperature. (I_A = specific flux of adsorbed molecules, p = pressure. x = surface concentration of adsorbed molecules).

If the rate of uptake were equated to the rate of migration, as suggested by Kennedy, the above would give

$dq/dt \propto q^2$ (assuming 'q' is effectively independent of pressure).

This is to be contrasted with the observed dependence, $dq/dt \propto 1/q$.

The expression derived by Smith and Metzner is considered to be a refinement of the more general, and well-established fact, that surface migration rates are increasing functions of coverage, at least at low coverage and under flow-conditions.

, It would therefore seem that initial rates of adsorption may not be identified with rates of migration expressed as fluxes. In fact, however, this is hardly surprising, for if a scheme is considered such as

$$O_2 + A \rightleftharpoons A.\,O_{2(s)} \xrightarrow{\text{migration}} B.\,O_{2\,(s)},$$

the rate of uptake is not determined by the flux of O_2 over the surface, but rather by the rate of uncovering of A sites.

In order that a molecule may migrate from A to B, it must become partially desorbed. It may then completely desorb and return to the gas-phase, or "jump" to a vacant B-site. If the oxygen is reversibly adsorbed at the A-sites as a charged species (e. g. O_2^-), it is possible to visualise this partially desorbed, charged molecule interacting with an oppositely charged centre (B site) at a distance 'd'. The coulombic force of attraction, F, will be determined by the inverse square law, i. e. $F \propto 1/d^2$.

Thus, the rate of uncovering of A sites may be said to be directly proportional to F, and hence to $1/d^2$.

Now, if the A-sites are imagined to be positioned at the centre of a series of concentric circles on whose perimeters lie B sites (and other A-sites), the distance 'd' that each molecule-ion must jump to its nearest unoccupied B-site will be determined by the number of blocked sites surrounding it. Thus the circular area swept out by 'd' will be proportional to some fraction of the total uptake 'q' at that time, assuming a uniform distribution of A and B sites over the surface.

Then, $\pi d^2 \propto q$

and therefore the rate of uncovering of A sites $\propto \frac{1}{d^2} \propto 1/q$.

Thus, if the migration is rate-determining

$dq/dt \propto 1/q$, which is the parabolic law.

The assumptions made in the above derivation are, however, numerous. Not least of these is the supposition that the numbers of A and B sites are constant. This may be true under conditions of steady-state illumination, but is unlikely to be true before electronic equilibrium is established, since at least one of the two types of site must be a source of photo-electrons.

As stated in Part 1, the photo uptake has been reported (13) to be subject to a small positive temperature co-efficient, and this was associated with a migration process of the above nature. Romero-Rossi and Stone (84), however, have since re-examined the sorption at low O_2 pressures ($P < 0.05$ mm), and report a negative co-efficient. These authors suggest this discrepancy may be explained again by a two-stage mechanism,

$$O_2 + \epsilon \underset{I}{\rightleftharpoons} O_2^-(s) \overset{\epsilon}{\underset{II}{\rightleftharpoons}} 2O^-(s)$$

They propose that, if II is rate-determining, then

$$E_A(\text{apparent}) = E_A(\text{true}) - Q_I$$

where E_A = activation energy, and Q_I = heat of chemisorption I.

Since Q decreases as the coverage increases, at low coverages $Q_I > E_A(\text{true})$ and $\therefore E_A(\text{app.}) < 0$; whereas at high coverages $E_A(\text{true}) > Q_I$ and $E_A(\text{app.}) > 0$.

The repeated appearance of O_2^- in schemes of the above nature is noteworthy. This is the surface species thought to result from the

fast, low-temperature uptake of O_2 on UO_2 (86). The adsorption sites were here considered to be U^{4+} ions. In general, it is thought likely by Charman et al (87) that when O_2^- is present on oxide-surfaces it will be reversibly chemisorbed, and hence more active catalytically than the more strongly bound O^-, or O^{2-} species.

In view of the prevalence of reaction-schemes of this kind, it may be worth-while to consider the kinetics that might be expected to result from an uptake mechanism represented by:-

$$\text{I} \quad O_2 + \epsilon \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2^- \qquad \text{II} \quad O_2^- + \epsilon \xrightarrow{k_2} 2O^-$$

This is identical to the Romero-Rossi scheme, except that II is considered to be irreversible, as suggested by conductivity data (4, 15).

The gas-uptake at time 't' must equal the total surface - oxygen, i.e. $q_t \propto (O_2^-)_t + (O^-)_t$ where ( ) = concentrations.

Now, $$\frac{d(O_2^-)}{dt} = k_1 P_{O_2} (\epsilon) - k_{-1} (O_2^-) - k_2 (O_2^-) (\epsilon)$$

and $$\frac{d(O^-)}{dt} = 2k_2 . (O_2^-) (\epsilon)$$

so that, if (ϵ), which represents the concentration of electrons available for photosorption, is assumed to be constant, then

$$\left.\begin{aligned} \frac{d(O_2^-)}{dt} &= A - B(O_2^-) \\ \text{and } \frac{d(O^-)}{dt} &= C(O_2^-) \end{aligned}\right\} \quad \begin{aligned} \text{where } A &= k_1 P_{O_2} . (\epsilon) \\ B &= k_{-1} + k_2 . (\epsilon) \\ \text{and } C &= 2k_2 . (\epsilon) \end{aligned}$$

The further assumption is made here that (ϵ) is the same in I and II.

Then, $\dfrac{d\,(O_2^-)}{A - B\,(O_2^-)} = dt$

and $t = \displaystyle\int_0^t \frac{d\,(O_2^-)}{A - B\,(O_2^-)}$

$\therefore \quad t = \dfrac{1}{B} \ln. \dfrac{A}{A - B\,(O_2^-)}$ if $(O_2^-) = 0$ at $t = 0$

i.e. $(O_2^-)_t = \dfrac{A}{B}\,(1 - e^{-Bt}) \qquad \ldots\ldots(1)$

Similarly,

$$\frac{d\,(O^-)}{dt} = C(O_2^-) = \frac{AC}{B}\,(1 - e^{-Bt})$$

$$\therefore\ (O^-) = \frac{AC}{B} \int_0^t (1 - e^{-Bt})\,dt = \frac{AC}{B}\,(t + \frac{1}{B}\,e^{-Bt} - \frac{1}{B}) \qquad \ldots.(2)$$

Thus $q_t = (1) + (2) = \dfrac{AC}{B}\,t + (\dfrac{A}{B} - \dfrac{AC}{B^2})\,(1 - e^{-Bt})$

which is of form $\underline{q = at + b\,(1 - e^{-kt})} \qquad \ldots.(3)$

Now, if it is assumed that step II is very slow compared with I, it can be shown that the constant 'a' in (3) is very small. For,

$$a = \frac{AC}{B} = \frac{A\,2\,(B - k_{-1})}{B} = 2\,A\,(1 - \frac{k-1}{B}) = 2\,A\,(1 - \frac{k - 1}{k_{-1} + k_2\,(\epsilon)})$$

Thus, if $k_2\,(\epsilon) \ll k_{-1}$, $a \doteq 0$

Equation (3) then reduces to

$$q = b\,(1 - e^{-kt})$$

or, rearranging, $b - q = b.\ e^{-kt}$

and $dq/dt = b\,k\,e^{-kt} = k\,(b - q). \qquad \ldots.(4)$

'b' represents the "uptake at infinity," and (4) is the expression found by Kennedy (2) to hold over the later stages of uptake. There is, however, little similarity between (3) and the parabolic, or Elovich equations.

The most important assumption made in the above derivation was that of the constancy of the electron-concentration. Although under normal photo-uptake conditions, electrons must be generated as the uptake proceeds, it is striking that no significant difference was observed between the kinetics under these conditions, and those under conditions of pre-illumination. The most natural conclusion is that the rate of excitation of photo-electrons is much greater than the rate at which they are removed by oxygen. The assumption would then be justified if the availability of the electrons to oxygen also remained constant as the reaction proceeded. Of course, here it is being assumed that step II can be represented by a true rate-constant, and is not migration-controlled, as considered before.

It is impossible to discuss the validity of such reaction-schemes without making reference to the electronic energy structure of the solid surface. Keeping in mind the picture of this structure presented in Part 1, the following electronic processes may be imagined to take place when the solid is illuminated with light of $\lambda = 3650\,\text{Å}$ (3.4 ev.):-

$$(A)\quad D \overset{h\nu}{\dashleftarrow\!\!\dashrightarrow} D^{+} + \epsilon_c \qquad (B)\quad \epsilon_c \rightleftharpoons \epsilon_t$$

where D=donor source, ϵ_c = conduction electron and ϵ_t = trapped electron.

It is supposed that $(\epsilon_c) \ll (\epsilon_t)$ at room-temperature, and that the recombination process $D^{+} + \epsilon_c \longrightarrow D$ does not take place to any great extent under illumination --- i.e. that the true life-time of an electron in the conduction band or trapping levels is much greater than that in the donor-levels. Thus, after ca. 2-3 hours' illumination, the situation is envisaged where virtually all the donors are ionised and a small constant concentration of electrons in the conduction band is in equilibrium with a much larger concentration of electrons localised at surface-traps. These traps are probably situated energetically just below the conduction band, and the electrons contained in the top-most levels may be raised thermally back into the conduction-band.

It has always before been assumed that when O_2 is adsorbed, it takes up electrons from the conduction-band, and thus destroys the photo-conductivity. Spectral evidence (e.g. 17, 18, 32), however, suggests the surface oxygen to be associated with the trapped electrons, with consequent removal of the absorption associated with transitions between the traps

and the conduction band. It is further proposed by Clark and Vondjidis (32) that, due to the high electron-affinity of oxygen, the traps are modified to deeper-lying levels. (After Wolkenstein (79)). The proposed situation is similar to that imagined to exist on illuminated Ag Br, in the photographic process.

This association of oxygen with the trapping levels is not inconsistent with the conductivity results, if the equilibria (A) and (B) are well displaced to the right. For then, removal of some of the trapped electrons, ϵ_t, will result in almost complete transfer of the conduction electrons to the traps. In fact, it is possible to imagine the conduction band as representing a kind of "over-flow" for the trapping-levels, and the latter may extend over a broad energy-range and be much more numerous than formerly supposed. The density of states must not, of course, be so high as to form a band.

The observed decrease in rate of uptake with increasing surface oxygen-concentration may also be explained by the trap-modification process. Although the electron-concentration may still be considered to be effectively constant in the early stages, the rate of transfer to the adsorbate will decrease as the energy of the traps falls to deeper and deeper-lying levels. This rate-decrease might be expected to be related exponentially to the energy-drop, and hence to the coverage. This proposal is merely an extension

of the ideas of Engel and Hauffe (88) where the rate of adsorption is considered to depend on electron transfer over an energy-barrier whose height increases with coverage θ, due to the increasing work function, Φ. Integration of the adsorption rate equation gave

$$\theta = k \log (1 + t/to) \qquad (k, \text{ to constants}),$$

which is a form of the Elovich equation. In the present instance, Φ would represent the distance below the conduction band of the quasi-Fermi level of the electrons in the trapping levels.

The two other chief aspects of the uptake - viz. the parabolic section and the H_2O-production, may both be associated with the migratory process discussed earlier. It is suggested that, in the early stages of uptake, electron-transfer at the localised electron-sources is fast, and that the rate of adsorption is controlled by the rate at which the resulting species (e. g. O_2^-, or O^- if dissociation occurs) migrate to other sites which are then oxidised, with the production of water. These sites may be labelled (after Bews) "oxidation sites." In the later stages, the rate is controlled by electron-transfer, as above, and, in fact, the migration process may by this time have terminated.

On this basis, it is not necessary to assume any stage of the uptake to be reversible, in order to explain the re-development

of photo conductivity when the gas is pumped out shortly after its admission (see P. 25). For, when this is done, the trapped electrons may be re-elevated thermally into the conduction-band, and the original conductivity will be restored, provided that (a) the number of such electrons is sufficient and (b) the traps have not been modified to levels too low-lying to permit thermal excitation.

A more difficult problem concerns the final nature of the sorbed oxygen. Several pieces of evidence led McLintock (4) to conclude that only the initially sorbed oxygen was catalytically active and, for example, capable of oxidising adsorbed hydrocarbon. It may be apposite, at this stage, to reconsider the situation regarding H_2O-production. If this H_2O does indeed result from a genuine photo-oxidation involving surface oxygen, and if the 2 : 1 molar ratio does represent the stoichiometry of the reaction, it must be concluded that virtually all of the O_2 taken up is eventually converted to H_2O, It would not, then, be expected that hydrocarbon subsequently adsorbed would be photo-oxidised.

Provisionally, then, many of the essential features of the O_2 uptake may be explained by the simple picture of irreversible interaction with a limited number of surface sites which act as acceptors, or 'traps' for lattice-electrons. These sites may

represent Kennedy's 'A' sites. Chemisorption is thus imagined to produce a negatively charged species which may then migrate to the so-called 'oxidation sites' where reaction leads to the production of H_2O, thus uncovering the original sites for further uptake of gas. This process will continue until all the oxidation sites are oxidised, or until the rate of electron-transfer becomes too low. In fact, according to Weisz (89), electron-transfer will cease when the Fermi-level of the solid coincides with the ionisation level of the adsorbate.

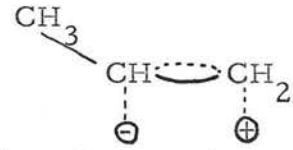
A truly comprehensive theory of O_2-sorption must be capable of explaining the observed effects concerned with pre-treatment, pre-illumination etc. presented in Part 3. Since most of the results were concerned with hydrocarbon sorption, this discussion will be continued after treating the latter uptakes in a way similar to the above. Indeed, it is hoped that, if it is possible to explain these results on the basis of the electronic transitions proposed here, more information may be gained on such topics as the physical nature of the donors, traps and "oxidation sites."

II. The uptake of C_2H_4 and C_3H_6.

It is logical to examine first the nature of the 'dark' olefin sorptions. With C_2H_4 this uptake was very small, but C_3H_6

was removed from the gas-phase in much greater quantities. This difference in the behaviour of the two gases may be associated with the polar nature of the C_3H_6 molecule, which can be described by

. In view of the essentially ionic nature of the free TiO_2 surface, the molecule might be imagined to adopt a "flat-on" configuration of the type



where ⊖ and ⊕ represent charged surface centres.

The binding must be considered to correspond to physical adsorption, or weak chemisorption, since the uptake was easily reversed by evacuation. The remarkable enhancement of the sorption by pre-sorbed oxygen (3 (II)) might be explained either by the removal of H_2O interfering with the adsorption sites, or by the increased concentration of negatively charged centres, if the oxygen is not entirely removed as H_2O as suggested in I. The similar increase caused by the presence of gaseous O_2 (3 (I)) must be associated with the very small dark O_2 uptake revealed only by conductivity measurements. Again, the removal of some form of constraint associated with surface water is indicated, though a small degree of oxidation may be involved.

In the non-polar case of C_2H_4, a dipole-induction effect may be concerned, or alternatively, the surface species might be

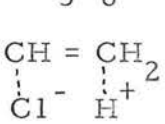
considered to be a weakly held π -complex of the type $CH_2 = CH_2$ with $\oplus$ where $\oplus$ could be associated with surface water, e. g. H_2O^+. In view of the lack of any increase in the uptake following O_2-sorption, the latter possibility seems more likely. The same π -bonding might well occur also with C_3H_6. In fact, it is worth-while to consider the nature, and possible influence of surface H_2O.

The most important structural aspect of any olefin in determining its chemical properties, is the negatively charged π -electron cloud which, in the absence of any other influence, renders the molecules electrophobic. Thus, since the free TiO_2 surface is essentially electro negative in nature, it might be expected that an olefin molecule would have to surmount an energy-barrier on its approach to the surface. Adsorption would not, therefore, be expected to take place at all readily at low temperatures. However, it is known (40) that the presence of adsorbed H_2O induces a positive surface charge in opposition to the expected negative one, and McLintock (4) has shown that H_2O -sorption is accompanied by electron-transfer to the solid. It thus seems likely that surface-water is present, at least in part, in the form H_2O^+ or some associated species. Indeed, it is possible, in view of the strong electric field expected at the solid-surface, that the sorption may be partly dissociative, to give H^+ and OH^-. Whatever

the exact nature of the binding, it is probable that, even after fairly extensive pumping at room-temperature, there still remains a considerable quantity of positively-charged water, which effectively neutralises the negative charge of the free surface, and permits approach of the olefin. In view of the obviously weak olefin-surface bond, it is natural to assume an equilibrium situation.

i. e. $R.CH = CH_{2(g)} \rightleftharpoons R.CH = CH_{2(s)}$

which is strengthened by the observed marked pressure-dependence of the propylene uptake. It may be recalled (3 (III)) that pre-treatment with HCl gas resulted in a large increase in the C_3H_6 sorption, the binding presumably being of the form



No corresponding increase was observed when the surface was treated with H_2O itself, but it is probable that most, if not all, of the H_2O sorbed at room-temperature is removed by subsequent evacuation. Gregg (62) has shown that surface-water is expelled only at temperatures close to those at which it was originally sorbed. Information on the influence of strongly chemisorbed H_2O could thus only be obtained by treatment at elevated temperatures. It is noteworthy that no dark uptake of either C_2H_4 or C_3H_6 was observed on films previously evacuated at 170° (4).

To conclude, it is proposed that the dark olefinic sorptions are made possible by the shielding effect of surface water, and a small equilibrium concentration of ethylene may exist weakly bound to the hydrated surface as a π-complex e. g. $CH_2 = CH_2 \cdots H_2O^+$ The same may hold for propylene, but in addition dipole interaction leads to a stronger bond, probably involving surface oxygen ions and positively charged H_2O.

Before discussing in detail the photo-uptake results of Part 3, it is of value again to consider briefly the results previously obtained by McLintock. Since some of the present observations were made on the same TiO_2 sample (A) as that of McLintock, any difference between the behaviour of the films in the two cases must presumably be due to the high temperature initial evacuation used by the latter.

In addition to observing no dark uptake of pure C_2H_4 or C_3H_6, McLintock reports (4, 15) no photo adsorption of C_3H_6 in the absence of presorbed O_2. C_3H_6/O_2 mixtures did show a dark sorption. Further, he found that the olefin photosorptions on oxygen-treated films were increased when the films were illuminated, or heated in vacuo prior to the uptake. This is to be contrasted with the pre-illumination results described in 3. (IV A).

It is natural to assume that such differences are again associated with surface water. It is particularly interesting to compare McLintock's pre-illumination results with those of IV B. If it is assumed that the only effect of pre-sorbing NH_3 is to dehydrate the surface, it would appear that pre-illumination of a 'dry' film results in an increase in C_2H_4 uptake, whereas the same procedure applied to a 'wet' film reduces the uptake.

A difference may exist between films evacuated at 170° and at room-temperature, other than simply one of degree of hydration. As a film temperature is raised, desorption of water from high-energy sites may be accompanied by re-adsorption at sites of lower potential energy (and hence higher energy of activation) (64). Thus, although the film is dehydrated by the treatment, such water as remains will be bound much more strongly to the surface, and may in fact be adsorbed at sites which normally participate in hydrocarbon-sorption. It is evident from McLintock's results that only the C_3H_6 uptake is affected in this way, and that photo-adsorption of O_2 regenerates activity.

It is difficult to interpret these results in the absence of knowledge of the nature of the sites involved, but it would seem that the process of O_2 sorption on such films created sites necessary for C_3H_6 photo-sorption, while at the same time increasing the

number of C_2H_4 adsorption sites. This provisionally suggests that more than one type of site is involved in the C_3H_6 uptake, and the fact that the sorptions mutually interfere (3 II) might be taken to mean that one of the sites is common to both hydrocarbons, though this effect could be due to steric hindrance.

These topics will be returned to later.

No significant conductivity changes were apparent (4, 15) when either olefin was admitted to a titania pellet in the dark, or under illumination, though a small degree of interaction with surface water was indicated in the dark. (See Part I). This led to the conclusion that the hydrocarbons interact with the positive holes produced at donor levels. Although, on the basis of the electronic processes proposed earlier (I), such an interaction would not lead to any conductivity changes under illumination, several problems are raised:-

(a) Following a C_2H_4 -photo uptake, it would be expected that the photo-electrons would be "stranded" in the conduction band and trapping-levels, so that the conductivity level attained during illumination should persist even after ceasing illumination. This was not found to be so, and since recombination could not take place to any great extent without desorption of C_2H_4, McLintock was forced to conclude that the conduction electrons were removed

by deeper traps, lying at roughly the same distance below the conduction band as the donor levels.

(b) In a similar vein, it is difficult to see why O_2 photosorption on a hydrocarbon-treated film should appear so similar to the untreated case. If this is to be explained by the idea of the deep-lying traps, it has to be assumed that electrons situated in these traps are capable of being photo-excited in exactly the same manner as are electrons bound to donors. This transition is again presumably supposed to utilise the same wave-length of radiation.

(c) Following an O_2 uptake, there should be a large concentration of positive-holes available to C_2H_4, and the gas should therefore be taken up in the dark, in amounts comparable with a normal photo-uptake. This was never observed, though it is worth noting that the present studies revealed a large increase in the dark C_3H_6 uptake under these conditions.

(d) It is impossible, on the basis of this simple theory alone, to account for the very great increase in hydrocarbon photo-uptake resulting from the pre-sorption of O_2.

Observation (d) has already been discussed briefly, and some connection between this activation and the water-production scheme proposed in I would seem to be indicated. Illumination in vacuo has been stated (19) to give rise to the evolution of H_2O, and the

evidence is that the H_2O is produced following a period of illumination, rather than during it. This is possibly also true in the case of O_2 uptake, and suggests some form of recombination process. Similarly, observation (c) leads to the conclusion that, following illumination in O_2, the original unionised donors are recreated, and, further, from (d), that these donors are either more "active," or more numerous than formerly. There is also a strong indication that these effects are linked with the activation/deactivation results associated with pre-illumination.

It is felt that most of these facts may be explained on the basis of the following generalised theory.

Other lines of reasoning have already led to the proposal that high-temperature treatment of hydrated TiO_2 results in a desorption/adsorption equilibrium where water becomes bound to sites of low potential energy. It is now proposed that these sites are in fact thermally ionised donors, or neighbouring centres which permit interaction with the latter. It may be assumed that the donor levels extend over a fairly wide range of energies i. e. "distances" below the conduction band, and that only the relatively high-energy sites become ionised thermally. If water interacts with these upper donor-levels, the positive holes may effectively be destroyed in forming a relatively strong bond. A species of this type will be referred to as D. X where 'X' is some form of water, not

necessarily = H_2O.

When a film in this reduced state of hydration is illuminated, the free donors D (which will lie at lower levels than the poisoned donors D. X) ionise in the usual way, and, on cessation of illumination, the electrons fall back into the donor levels. A recombination process takes place, freeing the bound water, and regenerating the free donors, i.e. $D.\ X + \epsilon \longrightarrow D + X^-$

Under these circumstances, then, illumination in vacuo followed by a dark stand, will increase the activity of a film towards C_2H_4.

When a 'wet' film is illuminated, however, desorbed water (probably originating from the trapping levels) may combine with the holes, in the same way as before i.e. $D^+ + X^- \longrightarrow D.\ X \ldots (1)$

In this case, however, the holes, being photo-produced, may lie at much deeper levels than in the thermal case. The exact distribution of combined donors among the energy-levels will depend on the relative rates of excitation, combination, and freeing of weakly held water, but the latter would be expected to adsorb at the sites of lowest potential energy available. In fact, after a long period of illumination, the donors may be almost entirely combined, provided that sufficient surface water was initially present. On cessation of illumination, it is suggested that electron-recombination takes place at the upper levels where the binding is

relatively weak, as before. This explains the evolution of H_2O following illumination. Water bound to the lower energy sites, however, will be strongly chemisorbed, and electron-recombination will not take place. Thus, following the illumination, a small number of the original donors are reformed, but a large number remain poisoned. The surface is thus deactivated towards C_2H_4.

The photo-uptakes of O_2 and C_2H_4 may also be understood on the above basis, if it is further assumed that photo adsorbed oxygen is capable of interacting with the poisoned donors. The latter may then be identified with the 'oxidation sites' proposed in I. It is not, however, intended to elaborate on the mechanisms of these sorptions at this point, beyond sketching a generalised outline of the reaction-sequences involved, since considerations concerned with the NO photo-uptake led to some important deductions regarding these mechanisms. It is therefore convenient to postpone a detailed discussion until the latter sorption has been examined. The following can, however, be said.

As O_2 photo sorption proceeds, two initial processes occur - electrons are removed from the trapping levels, and surface water (probably ejected from the traps) combines with the positive holes, producing the D. X species. Interaction between adsorbed oxygen, which will be written O_s^-, and the combined donors, may be described by equations of the type

(2) $D.X + O_s^- \rightleftharpoons D + XO_s^-$ and $XO_s^- \rightsquigarrow H_2O$

or, (3) $D.X + O_s^- \rightleftharpoons D.O_s + X^- \rightsquigarrow H_2O$

Equation (2) represents the case where there is a genuine photo-reaction, and (3) the case of simple displacement. In either case, the "oxidation" is expected to be a slow process, associated with migration, and hence the parabolic section of the uptake. Further, it is likely that the equilibria involved in (2) and (3) will be displaced to the left under illumination, due to readsorption.

i.e. $D \xrightarrow{h\upsilon} D^+ + \epsilon$ and $D^+ + X^- \text{ (or } XO_s^-) \longrightarrow D.X$

However, it can be seen that the end result of such processes is to return electrons to the solid that were initially removed from the traps. Thus, difficulty (c) is removed, and (d) may be explained partly on the basis of the following argument, and partly in terms of an extension of the theory which will be developed later.

During C_2H_4 photo uptake, again two processes occur - combination of C_2H_4 with positive holes, and combination of water with the same holes. A competition is thus set up between the olefin and surface water for available ionised donors. When O_2 is sorbed prior to the uptake, however, much of the surface water is removed, by (2) or (3), thus preventing, to a large extent, the poisoning reaction (1) from taking place during the olefin uptake.

Difficulties (a) and (b) may be resolved without recourse to the idea of deep electron-traps, though as will be seen later such traps

may in fact exist. For, on cessation of illumination, electron-recombination may take place to a limited extent with uncombined donors, high-energy donors combined with water (D. X) and, possibly to a small extent, with high-energy donors combined with C_2H_4 (D. C_2H_4). In addition, the surface traps may be sufficiently deep to accommodate the excess electrons. In any event, O_2 sorption on a C_2H_4-treated film would proceed initially utilising photo-electrons produced from the regenerated donors, the surface species so formed then reacting with both D. X and D. C_2H_4. Reactions of this kind will reproduce the original donors, and lead to rates of uptake faster than normal, and determined largely by the rate of readsorption of the products.

The above - enunciated theory is capable of explaining, at least qualitatively, most of the activation/deactivation facets of O_2 and C_2H_4 uptake. It is worth adding that the discontinuities observed in the C_2H_4 uptake curves (3 (I)) are also explicable, in that cessation of illumination leads to desorption of water bound to the higher energy donor levels. This idea is strengthened by the observed increase in the discontinuities in the presence of an absorbent such as NaOH.

The Kinetics of C_2H_4 uptake

It has been proposed that the kinetics of the O_2 photo sorption

proper are represented by the Elovich equation, $dq/dt \propto e^{-kq}$, and that the initial parabolic equation describes a rate-determining migration process associated with "oxidation".

The kinetics of hydrocarbon uptake were found to be predominantly Elovich in nature, but often the parabolic law appeared to be obeyed simultaneously with one or more Elovich expressions. It is unlikely that any appreciable surface-diffusion of the large olefin-molecules takes place, and in any case they have been assumed in the preceding treatment to be combined with localised positive holes. (The donors are taken to be localised for the reasons given in Part I). Some other interpretation of the parabolic kinetics must therefore be sought.

Adherence to this law was generally recognised by showing the linearity of the relationship $dt/dq \propto q + c$ (c const.)

Now, suppose an uptake follows the Elovich equation,

i.e. $dq/dt = a\ e^{-bq}$

Then, $dt/dq = \frac{1}{a} \cdot e^{bq} = \frac{1}{a}\left(1 + bq + \frac{b^2q^2}{2!} + \frac{b^3q^3}{3!} + \ldots.\right)$

$$= \frac{1}{a} + (b/a)\,q + (b^2/2a)\,q^2 + \ldots..$$

so that, if $(b/a)\,q >> (b^2/2a)\,q^2$ i.e. if $bq << 2$,

the expression reduces to

$$dt/dq = 1/a + b/a \cdot q$$

Thus, in the initial stages of an uptake, when 'q' is small, it can be seen that an Elovich-type expression might reduce, to a first approximation, to a parabolic expression, provided that 'b' is also small. In fact, 'b', which measures the rate of deceleration of the uptake, was found to be normally~0.1 for O_2 uptakes, and generally higher in the case of C_2H_4. This fits the observation that parabolic kinetics are associated primarily with O_2 uptake.

It must be stressed, however, that the above equations show only how the Elovich expression may approximate to the parabolic one. This does not necessarily mean that when the latter law holds it must represent such an approximation. However, it is suggested that this is so in the present instance, and that Elovich kinetics are truly characteristic of the process.

The question then arises as to the origin of these kinetics. According to the theory developed earlier, three basic reactions take place when TiO_2 is illuminated in ethylene. These may be expressed by the following equations -

$$D \xrightarrow{h\upsilon} D^+ + \epsilon \qquad \ldots\ldots(a)$$

$$D^+ + C_2H_4 \longrightarrow C_2H_4\,D^+ \qquad \ldots\ldots(b)$$

$$D^+ + X^- \longrightarrow D.X \qquad \ldots\ldots(c)$$

where D and X have their usual meaning. Reaction (b) may be written $D^+ + C_2H_4 \longrightarrow C_2H_4^+ . D$ if electron transfer takes place.

Now it is known that the growth of conduction electrons proceeds with a rate that falls off with time (e. g. (4),) but this may not necessarily be true for the growth of positive holes - i. e. reaction (a). In any case, however, the kinetics of uptake on pre-illuminated films, when these were large enough to permit analysis, were similar to the non-preilluminated case. This is taken here to suggest that the photo-generation of holes is fast compared with subsequent events, i. e. (a) is not rate-determining. In analogy with the ideas proposed for the O_2-sorption, it is suggested that the rate-determining step is the combination reaction (b).

The most usual interpretation of the Elovich equation is in terms of activated adsorption (88). The rate is supposed to fall off exponentially with coverage, due to the increasing energy of activation associated with electron-transfer through the space charge layer built up at the surface. The various "sections" of the Elovich kinetics - i. e. the lines in the log Rate vs q plots - are then associated with this process applied to different 'groups' of surface sites, each group having a successively higher initial energy of activation for adsorption.

There is another way of approaching the problem, however. If the initial adsorption is at the sites of lowest potential energy -

i. e. the lowest-lying donor-levels, and if the subsequent uptake involves combination with higher and higher-lying levels, then the strength of the C_2H_4 -surface bond should decrease as the adsorption proceeds, with an accompanying decrease in the heat of chemisorption. However, it is not easy to see why the rate should decrease exponentially with coverage, unless reaction (b) is reversible, and the evidence suggests it is not.

Exactly parallel considerations apply to reaction (c). The only part played by this reaction is thought to be the removal of sites active in the C_2H_4 uptake. The rate-laws governing the removal are unknown, but it is impossible to derive an Elovich-like expression on the assumption that reactions (b) and (c) may be described by true rate-constants. Any treatment following this approach leads to an expression similar to (3) in I, where the rate decreases exponentially with time.

(e. g. an expression of form $dq/dt = a\, e^{-kt} - b$ is obtained, assuming reaction (c) to proceed at constant velocity).

It is therefore thought that the observed kinetic behaviour must be attributed to the increasing difficulty with which electrons are transferred to, or shared with the solid; while preserving the idea that sites of lowest potential energy are occupied first. The height of the energy-barrier associated with the charge boundary layer may

increase more slowly than the Fermi level is raised by electron donation, which would give rise to a progressive decrease in heat of chemisorption. The existence of reaction (b) may explain why the C_2H_4 uptakes damped off more rapidly than the O_2 uptakes (and hence why the Elovich parameter 'b' was generally larger with C_2H_4.)

A final point that may be dealt with most conveniently in this section, is the question of pressure-dependence.

It was demonstrated (3. I) that, while O_2-uptakes showed little or no pressure-dependence under the prevailing conditions, C_2H_4 and C_3H_6 uptakes did show a fairly marked dependence, especially in the earliest stages following a pressure-increase. This may be understood in the light of the proposed reaction-schemes. Gaseous C_2H_4 molecules are supposed to interact directly with a fairly large number of surface-centres, and to act as donors of electrons to these centres. It is thus natural that the reaction-rate should be proportional to the concentration of the gas-donors. As the reaction proceeds, however, the rate falls, due both to the increasing coverage, and to the poisoning reaction (c). Any increase at this point of the (C_2H_4) : (X^-) ratio will favour reaction (b), and there will be consequently an increase in the rate of uptake.

In the case of O_2, however, the rate is initially controlled by surface migration from a limited number of sites. This is thus a zero-order, surface-controlled reaction. The first step, involving uptake at these sites, may well be pressure-sensitive, but the experimental conditions were such that the reaction was under way before the effect of pressure-changes was examined. In the later stages, however, the rates are determined by electron-transfer at the traps, the Elovich law applies, and the situation is analogous to the C_2H_4 sorption. It would be expected, therefore, that after prolonged illumination some pressure-dependence might be displayed. It may, however, be said that the "oxidation" D. $X + O_s \longrightarrow H_2O$ might well be suppressed at high pressures, the removal of H_2O from the surface being inhibited. The same may be true for the olefin-oxidations.

III. General.

As shown in Part 3, evidence was obtained for some form of relationship between the uptakes of O_2, C_2H_4 and NO, and a degree of site-sharing was indicated.

It was evident that the effect of pre-sorption of one of the gases on the uptake of another was not constant over the course of the second uptake - i. e. different stages of the sorption were affected to different degrees. As an illustration, Table 24 shows the

variation of C_2H_4 uptake with time on variously pretreated films. As can be seen, the ratio of uptake on an untreated film to that on NO-treated and pre-illuminated films, falls progressively with time. The ratio of uptake values on an O_2-treated film to the untreated values, however, passes through a maximum (see Fig. 32).

Similar considerations applied to the NO and O_2-sorptions.

The suggestion was, therefore, that during the early part of all the uptakes, similar surface processes, or sites, were involved, but that in the later stages the uptakes were impeded to a lesser extent, if at all. Since the electron, or hole-availability is expected to be the dominant factor in influencing the initial rates of any uptake, there is a strong suggestion that the effect of presorption is to alter the concentration of donors or trapped electrons. Once the sorption has proceeded for some time, other factors such as migration or electron-transfer may control the rates, and the effect will be minimised. There is also the possibility of site-regeneration as, for instance, in the case of O_2.

Little information can be gained from the results concerned with NO, until some conclusions have been drawn regarding the nature of the uptake itself.

The observation has been made (14) that the NO "uptake at infinity" is ca. 6 X the corresponding O_2 value. Now, on the

basis of the equation

$$3\,NO + \epsilon \longrightarrow N_2O + NO_2^- \qquad \text{(see 3. V.)}$$

only one surface site is occupied for every 3 NO molecules taken up, if N_2O is presumed to be released entirely to the gas phase, or to be merely physically adsorbed. Thus, if O_2 is supposed to be dissociatively adsorbed, it is possible that exactly the same number of sites are involved in both sorptions

$= 2.\,\Delta p_{\infty}\,O_2 = \dfrac{\Delta p_{\infty} NO}{3}$ Unfortunately, no conductivity measurements have been made during NO-sorption, but it is noteworthy that the reaction sequences proposed by Kennedy (2) bear a strong resemblance to the same author's proposed scheme for O_2-uptake. Both these schemes involve photo-electrons and holes.

The kinetics of NO sorption were shown (3. V) to be similar to those of O_2, and the observed parabolic section may again be indicative of an initially migration-controlled reaction. The chemical and physical similarity of the two gases is well known. Thus, both molecules are paramagnetic, and both may accept electrons fairly readily.

Many observations, then, tend to support the idea that the NO and O_2-photo sorptions are very similar. If NO is, in fact, associated with the surface traps in the same way as O_2, it is

possible to explain the formation of N_2O and NO_2^- by the following reaction-sequence:-

(1) $NO_{(g)} + \in_t \longrightarrow NO^-$

(2) $NO^- + NO_{(g)} \longrightarrow (N_2O_2^-) \longrightarrow N_2O + O^-$

(3) $O^- + NO_{(g)} \longrightarrow NO_2^-$

NO^- is the nitrosyl ion, known to exist in such compounds as sodium nitrosyl. The above scheme gives rise to the observed stoichiometry,

$$3\,NO + \in \longrightarrow N_2O + NO_2^- ,$$

and also explains the high pressure-sensitivity observed by Kennedy (2).

Both the observed kinetics, and the surface-deactivation towards C_2H_4-sorption are now explicable, if the NO_2^- species originally formed at the traps then migrate and interact with ionised donors,

e.g. $NO_2^- + D^+ \longrightarrow NO_2^-.\,D^+$, or $NO_2.D$.

This migration might then be rate-determining, if reactions (1) - (3) are fast, and parabolic kinetics will emerge. It is possible that the migration-step may take place earlier than postulated above - e.g. interactions (2) and (3) might take place at the donor sites, as,

$$D.^+\,NO^- + NO_{(g)} \longrightarrow D^+(N_2O_2)^- \longrightarrow D.^+\,O^- + N_2O$$

and $D.^+\,O^- + NO \longrightarrow D.^+\,NO_2^-$

If such a scheme has any validity, it is possible to extend these

ideas to the O_2 uptake itself. For example, reaction-sequences of the kind

$$O_2 + 2\epsilon_t \longrightarrow 2\,O^-$$

$$O^- + D^+ \longrightarrow D^+.\,O^-$$

or $$O^- + D.H_2O^+ \longrightarrow D^+.\,O^- + H_2O\uparrow$$

may be considered. If the last-written reaction is valid, it is easy to see why H_2O is produced by photo adsorption of O_2 in the maximum ratio of 2 : 1. For, once corrections are made for thermally and photo-produced H_2O, the reaction leads - to the displacement of one molecule for every O^- produced at the traps, and hence every $\frac{1}{2}$ molecule of O_2 sorbed, provided that every hole with which O^- interacts is bound to an H_2O molecule ion - i. e. provided sufficient surface water is present initially.

Before elaborating these arguments, it is necessary to consider the possible nature of the sites involved.

Nature of the donors and traps.

The proposals made in this section have been made on the assumption that TiO_2 exhibits n-type activity when irradiated at 3650 Å.

Photo adsorption data have again been interpreted in terms of localised electron-donors and surface traps, but it has been

necessary to assume a broad energy-distribution among these levels in order to explain the kinetics of uptake, and a variety of subsiduary effects associated with pre-illumination, pre-sorption etc. This situation is supported by spectral evidence (e. g. 17, 32) and by the observation (62) of a wide range of energies involved in water-to-surface bonds, and may be ascribed to the essentially heterogeneous nature of the surface.

Any attempt at identifying the centres involved is hindered by lack of unambiguous evidence regarding the nature of the surface. However, the active centres must be associated with the impurity levels of the solid, and hence with non-stoichiometry. The usual entities considered are ... (1) anion-vacancies, which may be represented $(Ti^{3+}. Ov. Ti^{3+})^{o}$ (2) interstitial cations, e. g. Ti^{3+} (3) centres due to the incorporation of foreign ions, e. g. chloride and (4) other lattice imperfections, e. g. dislocations, Frenkel defects etc.

The corresponding electron-releasing and trapping processes could then be written

(1) $(Ti^{3+}\ Ov\ Ti^{3+})^{o} \underset{+\epsilon}{\overset{-\epsilon}{\rightleftharpoons}} (Ti^{4+}\ Ov\ Ti^{3+})^{+} \underset{+\epsilon}{\overset{-\epsilon}{\rightleftharpoons}} (Ti^{4+}\ Ov\ Ti^{4+})^{2+}$

(2) $Ti^{3+}_{(i)} \underset{+\epsilon}{\overset{-\epsilon}{\rightleftharpoons}} Ti^{4+}_{(i)}$ (3) $Cl^{-} \underset{+\epsilon}{\overset{-\epsilon}{\rightleftharpoons}} Cl$

It is appropriate at this stage to take account of the quantities involved in the uptakes, in terms of surface coverage. Taking the

surface area as 100 $m^2\ g^{-1}$, and the ionic radii of Ti^{4+} and O^{2-} as 0.64 Å and 1.32 Å respectively (2), it is easy to calculate the number of surface ions, assuming a uniform stoichiometric surface. Such a calculation gives $(Ti^{4+}) = 8.2 \times 10^{20}$ ions/g and $(O^{2-}) = 1.6 \times 10^{21}$ ions/g.

Now, the total adsorptive capacity of the TiO_2 samples examined by McLean (3) for O_2, was reported by that author to be $\Delta p_\infty = 170\ \mu$moles g^{-1}. Assuming dissociative adsorption, this corresponds to 2.0×10^{20} surface O^{-} s/g, which is ca $\frac{1}{4}$ of the total number of surface Ti^{4+} ions. It should be said that this quantity is much greater than the O_2-uptakes observed in the present instance, which were normally $\sim 50\ \mu$moles g^{-1}. However, it is informative to consider estimates of the possible concentration of imperfections with the above quantities in mind. Since non-stoichiometry is associated in TiO_2 primarily with oxygen-deficiency, it is particularly apposite to estimate the concentration of oxygen-vacancies, or titanium interstitials present. Taking a sample represented by $TiO_{1.95}$, the concentration of oxygen-vacancies can be calculated to be $4.0 \times 10^{19}\ g^{-1}$, or 66 μmoles g^{-1}, or less if the presence of Ti interstitials is also included. Since higher $Ti^{4+} : O^{2-}$ ratios cannot be considered without entering into the region of blue, reduced titania, the quantity 66 μmoles must represent an absolute maximum,

unless the surface concentration of vacancies is much greater than the bulk concentration. The same considerations apply to interstitial titanium ions.

The only other entity specified earlier was lattice chloride. The total chloride concentration, estimated by HCl - evolution (3. III), was found to be $\sim 84\ \mu$moles g^{-1}. Much of this chloride must undoubtedly have been present on the surface, and since surface-sorbed Cl^- has been shown to exert no activating influence on the oxide (3. III and (19)), it must be considered unlikely that lattice-chloride is present in sufficient quantity to represent donor, or trapping-levels.

It is, however, difficult to estimate the probable concentration of the surface-traps. For, while arguments based on conductivity results might predict these to be only slightly less numerous than the donors (see I), kinetic considerations in terms of migration have usually led to the conclusion that the sites for initial O_2 uptake are much less numerous than the sites for final adsorption. In addition, several complicating factors exist - viz. (a) each trap may be capable of accommodating more than one electron (b) the possible existence of deep-lying traps, already mentioned in II, and (c) the possibility of sorbed oxygen returning electrons to the solid, according to reactions of the kind $D^+ + O^- \longrightarrow D.O$.

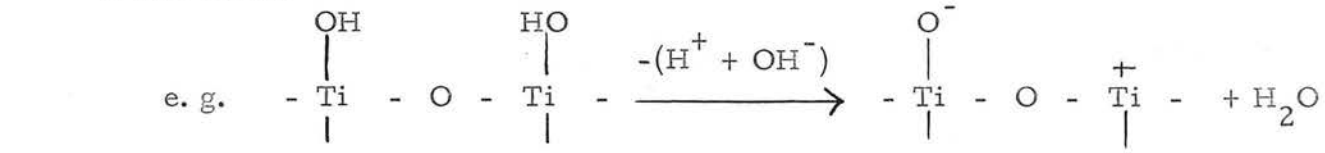
This might mean that the same traps could be utilised repeatedly during uptake.

It is felt that these difficulties may be largely overcome if the trap-concentration is indeed much lower than the donor concentration, while only relatively few of these donors are free to ionise. It will be seen later that the proposed nature of the donors is in accord with a large number of these being poisoned by surface water, and that O_2 sorption may regenerate activity.

It is, therefore, proposed that the traps participating directly in O_2 photo sorption be identified with oxygen-vacancies, possible present in quantities approximating to 50 μmoles g^{-1}, and therefore capable of accommodating $\sim$100 μmoles electrons / g. The vacancies may be distributed over a relatively large energy-range, due to surface-heterogeneity, their presence on different crystal faces or in rutile or anatase-type lattice structures, etc. Doubly ionised vacancies are expected to lie at levels lower below the conduction-band than singly ionised centres. Each trap may be utilised more than once during O_2 -sorption, due both to double electron-occupancy and to oxygen feeding electrons back to the solid through the donor-levels. The kinetics will thus be governed by parabolic migration away from a small number of high potential-energy sites, until the rate at which electrons are returned to the

solid becomes too low to maintain an approximately constant trap-Fermi-level.

One type of defect which was not listed earlier, and which is specific to the surface, is the hydroxyl-vacancy. Since TiO_2 is imagined to be formed by dehydration of $Ti(OH)_4$, the surface would be expected to carry a large number of OH groups, and this is borne out by spectroscopic observations (e. g. 22, 61). When vacancies exist they might be considered to occur in pairs, due to water-loss,



Formally, the effect of an elimination of this kind is to create a $Ti^{4+}.O^-$ entity, and a neighbouring Ti^{4+} ion which carries a net positive charge. The latter species has a co-ordination number one less than the normal, and might, then, be expected to represent a discontinuity in the lattice periodicity, and may in fact constitute a deep trapping level for electrons thermally released from oxygen-vacancies, or donated by molecular water.

The $Ti^{4+}.O^-$ entity may itself represent the light-absorbing species. Thus absorption of a light-quantum may result in electron-transfer from the oxygen to the titanium ion,

i. e. $Ti^{4+}.O^- \xrightleftharpoons{h\nu} Ti^{3+}.O$

this representing access to the conduction-band, and generating

what is in effect a free-radical. A similar transition has, in fact, been suggested (54) to occur within the lattice, and to be responsible for certain absorptions observed in the quartz ultra-violet (see Part I). If such surface-transitions do correspond to the 3650 Å absorption, the donors previously referred to as 'D' must be identified with surface O^- associated with hydroxyl-vacancies.

The conduction electrons so generated become largely trapped at oxygen-vacancies, which are, therefore, in thermal equilibrium with the conduction-band

e.g. $Ti^{3+} + \left[Ti^{4+}.O_{v.}\ Ti^{4+}\right] \rightleftharpoons Ti^{4+} + \left[Ti^{3+}.\ O_v\ Ti^{4+}\right]$

Much of the previous discussion relating to the behaviour of the donors and traps may still be considered to apply; with the important difference, however, that the final sites for O_2 sorption cannot now be identified with the donors themselves, but rather with the neighbouring Ti^{4+} ions. When uncombined, these ions must represent positive holes, but it is highly likely that at 27°C. those not acting as electron-sinks for O^{2-}-vacancy electrons, will carry adsorbed water, with resultant loss of positive-hole character. The binding is probably through the oxygen lone-pair,

i.e. $(Ti^{4+})^+ + H_2O \rightleftharpoons Ti^{4+} \leftarrow H_2O^+$

An estimate of the degree to which the active centres are hydrated may be obtained from the results of Ritchie and McLean (14),

who studied NH_3 uptake on TiO_2 films previously evacuated at ca. 10^{-4} mm. for periods of up to 5 days. These authors found the average concentration of H_2O capable of being thermally replaced by NH_3 to be 649 μmoles g^{-1}.

Now, if it is assumed that the only donors which are free to ionise are those adjacent to titanium ions which accommodate electrons originating at oxygen-vacancies, then

$$N_{Df} = 2 N_T \quad \text{and} \quad N_s = N_D - 2 N_T$$

where N_T = concentration of traps (i. e. O^{2-} vacancies), N_D = total concentration of donors, N_{Df} = conc. of free donors, and N_s = conc. of O^- adsorption sites, which are here considered to be those Ti^{4+} ions carrying adsorbed H_2O. Thus, if the oxygen taken up at infinity (= 170 μmoles/g.) is supposed to be present partly at the traps, and partly at the sites for final sorption

$$340 = N_s + 2N_T = N_D.$$

Now, if every active centre other than the Ti ions carrying trapped electrons, is capable of accommodating H_2O, and if, further, each trap may carry two H_2O molecules, then the total H_2O concentration will be given by

$$2 N_s + N_{Df} + 2 N_T = 2 N_s + 4 N_T = 2 N_D = 680 \ \mu\text{moles/g}$$

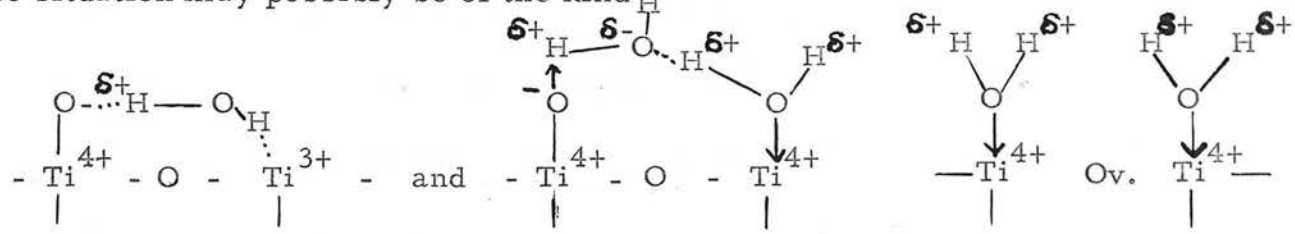
which is higher than the average value obtained by McLean and Ritchie, but is of the right order of magnitude. If each trap may accommodate only one H_2O molecule,

$$2N_s + N_{Df} + N_T = 2N_D - N_T = 649,$$

giving $N_T = 31$ μmoles/g.

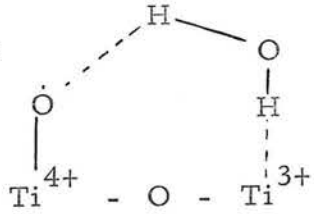
which is of the expected order of magnitude for the concentration of O^{2-} vacancies.

In any event, it would seem that at least some of the "free" donors must accommodate one H_2O molecule, and that the other donors plus their neighbouring Ti^{4+} ions must accommodate two. The situation may possibly be of the kind



'Free' donor | Inactive donor (oxygen site) | Occupied trap

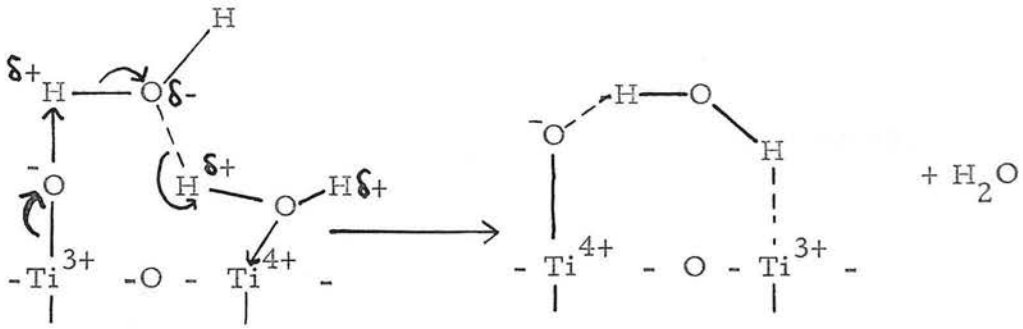
where the water-surface bond is either through the oxygen lone pair, or through hydrogen-bonding of the same kind found in liquid water. The deactivation effect caused by pre-illumination may be due to desorption of H_2O bound to the traps and readsorption at active donor sites, the binding under illumination presumably being of the form



Such "3 - electron" hydrogen bonds are known to exist in aqueous oxygen solutions (90).

The release of H_2O following illumination (see I) may be due to trapping of conduction electrons by poisoned donors,

e. g.



Similarly, O^- species resulting from O_2 uptake at the traps must be capable of migrating to, and interacting with, centres of the above type, with the production of H_2O, and the creation of a new Ti^{4+}. O^- species which may then ionise under illumination in the normal way. The mechanism governing this process may be complex, or may involve simple displacement. The net result may be written.

$$D^oH_2O \quad H_2O^+ \quad S^o + O^- \longrightarrow D^oH_2O + D^o + H_2O$$

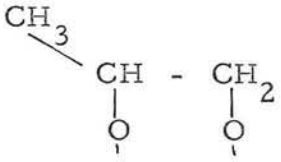
where 'S' = oxygen - sorption site (i. e. Ti^{4+})

On this basis, therefore, the effect of photosorption of O_2 is not only to remove water, but also to create new donors.

It is now possible to return to the general discussion relating to the NO and hydrocarbon uptakes.

If the idea of olefin interaction with positive holes is to be preserved, the new approach to O_2-uptake leads to the conclusion that the sites for olefin uptake are surface O. species produced

by illumination. It is suggested that C_2H_4 may utilise only one such site, and the binding may be represented - $C\bar{H}_2 - \bar{C}H_2$ - O. Ti^{4+} where there is a partial opening of the double bond. C_3H_6, on the other hand, probably becomes bound to two such sites as,



Since the distance between the two titanium ions comprising the vacancy can be calculated to be 3.92 $\mathring{A}$, and the C - C distance in saturated aliphatics is 1.54 $\mathring{A}$, a geometric factor is here introduced, limiting the extent of the uptake. It is worth recalling (3 II) that presorption of C_3H_6 was more efficient in reducing a subsequent C_2H_4 uptake, than vice-versa. The dark sorption is again considered to involve surface oxygen and water, the oxygen concerned now being identified largely with unionised donors (i. e. O^-).

It is less easy to interpret the results concerned with NO sorption, due to the additional complexities involved. It is again suggested that the final sites for nitrite are identical to the oxygen sites ('S'-sites), but if this is so, either a species such as NO^- or NO_2^- must be capable of displacing H_2O^+, or the migrating species is O^- and step (3) in the scheme proposed earlier, takes place at the S-sites. Further, there seems no reason why a

reaction such as

$$NO + O. \longrightarrow NO_2 \qquad (4)$$

should not take place. Indeed, it may be necessary to assume that this reaction does occur in order to explain the uptake on O_2 treated films. If direct combination of the gas with the donors does accompany the other reaction sequence proceeding through the traps, it may be valid to assume that reaction (4) takes place to approximately the same extent as the C_2H_4 uptake. That is, a pressure-decrease after 60 mins. of ca. 75 divs $\equiv$ NO uptake of 75 x $^4/_3$ = 100 divs. (see 3 V), and if approx. 9 divs. is taken up directly at the donors, the total nitrite formed = $(\frac{91}{3} + 9)$ divs. $\simeq$ 39 divs. and N_2O formed = $\frac{91}{3} \simeq$ 30 divs. Thus $NO : N_2O : NO_2^-$ = 3 : 0.9 : 1.2 which is in reasonable agreement with the results of McLean & Ritchie, of 3.0 : 0.85 : 1.02.

It is therefore proposed that the uptake scheme be amended to:-

$$\begin{array}{lccccc} & NO & \xrightarrow[(1)]{\epsilon} & NO^- & \xrightarrow[(2)]{NO} & N_2O + O^- \\ (4) & \downarrow -O\cdot & & & & \downarrow \text{migration to S-site} \\ & -NO_2 & \xleftarrow[(3)]{NO} & S.O. & \longleftarrow & S.O^- \end{array}$$

Reaction (4) will take place to an extent determined by the concentration of free donors, and by the surface coverage, as with C_2H_4.

Similarly, O_2 uptake on NO-treated films must proceed partly through utilisation of sites not occupied by nitrite, and partly through interaction with the latter either to form nitrate or to result in displacement of NO_2^-. The latter possibility seems the more likely one since the uptake was often greater than on untreated films. This is not to suppose, however, that such a displacement leads to the formation of free donors - it is likely that the displaced NO_2^- ion remains localised at the oxygen-site, and may form what would be effectively a peroxonitrite ion $(O = N - O - O)^-$s.

Although the results of 3 V may thus be explained qualitatively, the processes involved are obviously highly complex. Any attempt to place them on a quantitative basis must, therefore, represent only an approximation to the true situation. One of the major problems here is a lack of any absolute measure of the total adsorptive capacity of the films. The "uptake at infinity" values quoted earlier were obtained by McLean on the assumption that linear extrapolation of 'Rate vs. uptake' plots to zero rate, gave such a measure. In the present studies, the later stages of uptake were best represented by a logarithmic plot, so that no similar extrapolation could be made. In any case, it is doubtful whether such an extrapolation could be justified, in view of the

heterogeneous nature of the surface.

However, it is felt that the following semi-empirical approach does at least add strength to the proposed mechanisms, and perhaps indicates trends which remain to be explained.

Consider C_2H_4 photo-uptake on 0.100 g of an untreated TiO_2 sample.

Suppose that the uptake, 'q' divs., after 60 mins. is directly proportional to the number of free donors, 'N'

$$\text{i.e.} \quad q = k.\ N \qquad (1)$$

The water-combination reaction, previously written as $D^+ + H_2O \longrightarrow H_2O^+ D$ is here supposed to be of secondary importance over such a short period of illumination.

Now, the activating influence of presorbed O_2 represents an unknown quantity, but if the activation resulting from the uptake of ' x' divs. is considered to be due to the creation of A. x new donors (A const.) all of which are free to ionise, the C_2H_4 uptake may be expressed as

$$q = k\,(N + A\,x) \qquad (2)$$

Similarly, the deactivation due to NO presorption may be written

$q = k\,(N - B\,y)$ where y = the pressure decrease observed in NO. 'B' must reflect the fraction of NO molecules

taken up which interact with the donors, and it was previously suggested that during a pressure decrease of 75 divs. over 1 hr., ca. 9 divs. were taken up in this way. 'B', therefore, may be equated approximately to $^3/_{25}$, provided that 'y' represents the pressure decrease observed over 60 mins. Therefore we have,

$$q = k\left(N - \frac{3}{25}\, y\right) \qquad (3)$$

Now, substituting representative results selected from Table (3), Sec. V, we have :-

(1) untreated TiO_2 $\quad 9.0 = k\,N$

(2) O_2-treated " $\quad 17.5 = k\,(N + 11.5\,A)$ } sensitivity = 0.050 mm div^{-1}

(3) NO " " $\quad 3.0 = k(N - 12.2)$ }

Solving for 'k' and 'N' from (1) and (3) gives

$\underline{k = 0.49}$ $\qquad$ $\underline{N = 18.4}$

And substituting these values in (2), gives $\underline{A = 1.5}$

The fact that $A \neq 2$ may be attributed to poisoning of original, or newly created donors by surface H_2O.

Further examples were chosen from Table (3) and predicted 'q' values calculated from equations (1) - (3). When two pre-treatments were involved, the procedure was as follows:-

(a) When NO was sorbed on an O_2-treated film, it could no longer be assumed that B = $^3/_{25}$. In fact, it was found that good agreement between q calc. and q obs. was obtained if the

initial O_2 -sorption was ignored, and the calculation made as for an untreated film.

(b) When O_2 was sorbed after NO, a small reactivation was apparent, presumably due to O_2 uptake at sites unoccupied by nitrite. A new 'A' value was obtained by substituting the results of example (b) below, giving A = 0.30. The q calc. value shown in brackets in ex. (b) is that obtained purely from NO-deactivation, i.e. assuming A = O.

	Pre-treatment (divs)	q obs	q calc.
(a)	1. NO (Δp 26.5)	7.0	7.4
(b)	1. NO (Δp 75.8) 2. O_2 (14.1)	6.6	(4.6)
(c)	1. O_2 (16.0) 2. NO (Δp 77.8)	4.3	4.5
(d)	1. O_2 (1200 m. ill$^{n.}$) 2. NO (Δp 79.6)	3.2	4.3
* (e)	1. C_2H_4 (9.0) 2. NO (Δp 101.3) 3. O_2 (13.9)	5.5	5.1 *

* (e) was computed on the assumption that NO and C_2H_4 adsorbed independently of one another, and that A = 0.30 (see above). The total deactivation due to C_2H_4 and NO was taken to be the same as that which would have resulted from NO uptake alone if the latter had taken place over 1 hr's illumination.

The agreement between q calc. and q obs. in the above table is surprisingly good, in view of the complexity of the processes, and the approximations made. It may be noted that in ex (a) improved agreement can be achieved by taking into account the fact that the initial illumination in NO was for only 13 mins., and not 60 mins. Substituting a typical value for C_2H_4 uptake after 13 mins. for $\frac{3}{25}$ y gives q calc. = 6.8.

The most serious problem presented is the apparent complete lack of activation when O_2 is presorbed before NO. It is indeed expected that the amount of NO combining with the donors will be much greater than normal under these circumstances, but it is easily shown that the extent of the deactivation requires such an amount to be greater than the normal C_2H_4 uptake on O_2-treated films. For example, in (c) above, 34 divs of NO would be required to be taken up at donor centres. Although this is not impossible, a very high 'B' value is implied, and there are at least two other possibilities. - (1) interaction between nitrite and neighbouring donor sites could lead to deactivation of the latter, or (2) it is possible to imagine a reaction scheme slightly different from formerly. If uptake at the donors and at the traps takes place simultaneously,

i.e. if $NO \xrightarrow{(1)} NO^- \xrightarrow[(2)]{NO} N_2O + O^-$

and $NO + S\,O. \xrightarrow{(4)} S.\,NO_2$

then O^- may diffuse to the S - sites and displace nitrite, as has been supposed to occur when O_2 is sorbed on NO-treated films.

i.e. $O^- + S.\,NO_2 \longrightarrow S.\,O.\,NO_2^-$

Since the surface is largely covered with oxygen, this reaction may predominate over the normal uptake at unoccupied S - sites. In either case, however, 3 moles of NO are taken up with the production of 1 mole nitrite and N_2O, and, if the above sequence does predominate, with the destruction of 1 mole of donor sites. In ex (c), the NO uptake is $\frac{4}{3}$ x 77.8 = 104 divs and 104/3 = 34.7 divs is almost exactly the required deactivation.

It may be significant to examine briefly the meaning that is to be attached to the quantity 'N', found to be 18.4 divs. This value is supposed to represent the total number of free donors normally present on 0.100 g of 'untreated' TiO_2, assuming one C_2H_4 molecule is adsorbed per donor. In molar terms this is equivalent to $\frac{18.4 \times 0.05}{760} \times \frac{58}{22400} \times \frac{273}{300}$ moles,

or 28.5 μ moles g^{-1}.

This quantity was previously equated to 2 N_T : but if, instead, N_{Df} is taken to represent the number of donors not combined in any way with molecular water, then the total

concentration of water is given by

$$(H_2O) = 2N_S + (2N_T - N_{Df}) + 2N_T$$

$$= 2N_D - N_{Df} = (680 - N_{Df})\ \mu\text{moles}\ g^{-1}$$

And, (H_2O) was found by McLean and Ritchie to be ca. 649 μ moles/g, so that $N_{Df} = 680 - 649 = 31\ \mu$moles/g, which is in excellent agreement with the above estimate of 28.5 μ moles/g.

The Olefin oxidations

It is not intended to enter into any detailed discussion of the mechanisms involved in the oxidations, since the appropriate experimental results were here incomplete. It is, however, suggested that the reactions take place along the general lines:-

$$O_{2\,(g)} \rightsquigarrow S\,O\cdot$$

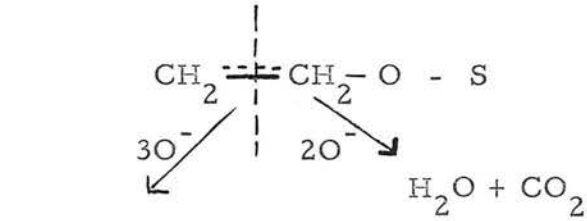
$$H\,C + n\,(SO) \longrightarrow (n\,SO)\,(H\,C) \xrightarrow{x\,O^-} n\,S\,O + \text{reaction products}$$

where "H C" = hydrocarbon, and n = 1 with C_2H_4, and 2, with C_3H_6.

i.e. attack by O^- takes place at donors combined with olefin, regenerating the original donors, or, if the latter are destroyed in the photo reaction, providing sites for the further uptake of oxygen.

It may be seen that the stoichiometry observed by McLintock (4) for the C_2H_4 oxidation can be derived by assuming attack of 5 O^-'s at 1 C_2H_4 -O site.

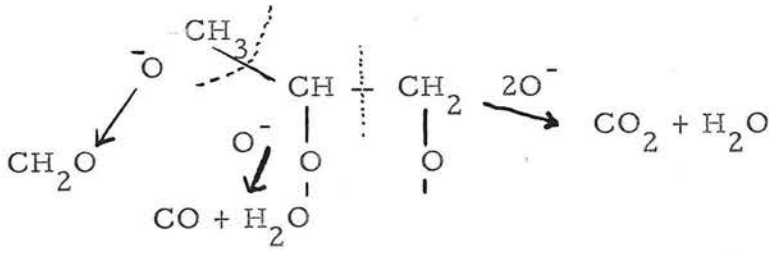
e. g.



i. e. $C_2H_4 + 3O_2 \longrightarrow 2\,H_2O + 2\,CO_2$

assuming that the donors are utilised in the reaction, and that the original free donor-concentration is << than the amount of O_2 sorbed.

The situation regarding C_3H_6 is more complex. If the possible presence of both CO and formaldehyde in the reaction-products is admitted, then a similar scheme might be proposed:-



i. e. $C_3H_6 + 3O_2 \longrightarrow CH_2O + CO + 2\,H_2O + CO_2$

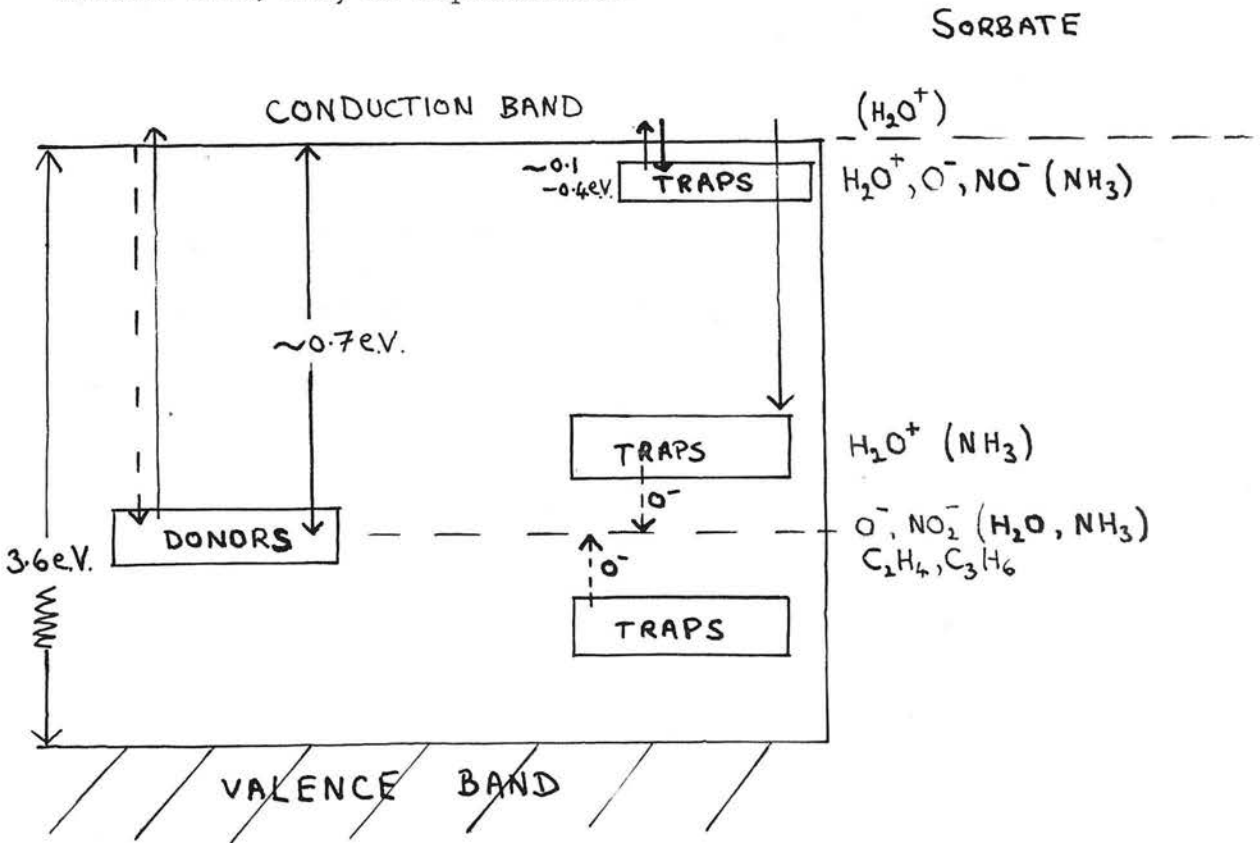
It may be said that no evidence was obtained in the present instance for the presence of surface CH_2O, and it is possible to suggest as one of the many alternatives to the above scheme, a process of partial oxidation involving retention by the solid of acetaldehyde, or acetic acid.

CONCLUSION

The adsorption mechanisms proposed here have involved interaction of gas and sorbate phase molecules or ions with three different kinds of active sites - electron donors, 'shallow' traps and deeper-lying trapping centres associated with molecular water. The shallow traps have been tentatively identified with oxygen-vacancies, and the donors and deep traps with hydroxyl-vacancies. The band-structure of the solid-surface may be modified to include the deep traps, or sinks, which may lie just above or below the donor levels, depending on the exo- or endo- thermal nature of the reaction

$$S^+ + O^- \longrightarrow S^+.O^- \equiv D^o$$

The energy-levels, along with their possible associated sorbate ions, may be represented:-



The above energy-values are based on optical data (e.g. 52, 17, 32, 18), but their assignment to specific electronic transitions must be considered to be speculative. Further information on the distribution of trapping levels could be obtained from a study of the temperature-dependence of the photoconductivity, and it might be possible to combine such measurements with thermogravimetric analysis of the H_2O sorption isobar.

Interpretation of the photo-adsorption data has here been in terms of an overall scheme which is basically a compound of previously suggested ideas. For example, the 'A' and 'B' - site concept of Kennedy (2) has been largely retained, including the migration-controlled O_2 uptake mechanism, though the proposed nature of the donors and "oxygen sites" is more akin to the ideas of McLean (3). Similarities also exist to the other reaction schemes of McLintock (4) and Bews (17): but it is felt that the present scheme is more comprehensive than formerly, being capable, for example, of embracing many diverse features of the interrelated oxygen, hydrocarbon and nitric oxide uptakes. No claim is made, however, to have provided a unique explanation of the intricacies involved in the photosorptions. It is merely suggested that the treatment described in the previous

pages serves as a reasonable account of the electronic processes that may occur within the surface layers under illumination. Proof that these processes do occur is not possible at the present level of experimental investigation, but some degree of confirmation may have been achieved from the quantitative approach towards predicted C_2H_4 uptake values, and free donor concentrations.

Future investigation might be directed at elucidating the nature of the finally sorbed species. For example, infra-red A.T.R. techniques might be developed in order to examine the hydrocarbon-surface bond, and the possible presence of CH_3 groups on ethylene-covered surfaces. Magnetic susceptibility measurements could well provide valuable information on the concentration of paramagnetic centres (e.g. $O^{\cdot}$) in the dark, under illumination, and in the presence of various adsorbates, and hence might settle the nature of surface oxygen. Extension of photoconductivity measurements of the type made by McLintock (4) to include a study of the NO sorption would also be of interest, and the origin of photodesorbed H_2O might profitably be examined, using labelling techniques.

TABLE 1 (Fig.14)

O_2 - adsorption on untreated TiO_2 (Sample B)

O_2 - pressure = 51.7 mms.

Bourdon sensitivity = 0.050 (3) mm./div.

	t(mins.)	ΔR(divs.)	Δp(divs.)	t	Δp	
Light on	0	0	0	210	19.0	
	0.5	1.9	0.7	240	20.2	
	1	3.3	1.1	255	20.5	
	2	5.6	1.8	285	21.8	
	3	7.1	2.3	300	22.2	Light off
	5	9.7	3.1			
	10	14.0	4.6			
	15	17.3	5.7			
	20	20.0	6.6			
	30	24.8	8.3			
	42	27.2	9.2			
	50	30.1	10.2			
	60		11.2			
	75		12.5			
	90		13.5			
	105		14.2			
	135		15.9			
	150		16.5			
	180		17.9			

TABLE 2 (Fig.14)

C_2H_4 on untreated TiO_2 (Sample B)

C_2H_4 pressure = 48.7 mms.

Bourdon sensitivity = 0.050 (3) mm/div.

	t(mins.)	ΔR(divs.)	Δp(divs.)	t	Δp
	0	0		39	9.0
	0.5	0.8		54	9.9
	1	1.0		69	10.7
	2	1.3			
	5	1.6		84	11.3
	10	1.8		99	11.8
	15	1.8		114	12.4
Light on	0	0	0		
	0.5	4.2	1.3	129	12.9
	1	6.0	1.9	144	13.3
	2	8.9	2.9		
	3		3.4		
	5		4.1		
	10		5.5		
	15		6.3		
	20		6.8		
	25		7.3		
	30		7.8		

TABLE 3 (Fig. 17)

C_2H_4 on untreated TiO_2 (Sample A)

C_2H_4 pressure = 55 mm.

	t(mins)	ΔR (chart divs)	t	ΔR	
Light on	0	0	445	94.0	
	1	7.5	505	97.2	
	5	27.0	550	98.5	
	10	40.5	600	101.8	
	20	50.8	625	103.5	(overnight
	30	54.8	630	104.0	break)
	50	58.4	635	104.5	
	60	59.8	645	105.5	
	120	66.2	655	105.8	
	180	69.7	665	107.0	
	240	72.0	680	109.2	
	265	74.0			
(overnight	270	74.7			
break in	310	81.7			
illu[illegible])	340	86.0			
	355	87.7			
	375	90.0			

TABLE 4 (Fig. 17)

O_2 on untreated TiO_2 (Sample A)

O_2 pressure = 50 mms.

	t(mins)	ΔR (chart divs)	t	ΔR	
Light on	0	0	221	86.9	
	1	6.8	235	88.2	
	5	19.8	250	89.7	overnight
	10	28.7	252	90.7	break
	20	38.9	255	91.2	
	30	46.1	260	92.0	
	45	54.0	270	93.6	
	71	63.1	280	94.5	
	105	72.1	300	97.5	
	125	76.4	325	99.0	
	150	79.3	370	102.5	
	180	83.2	430	106.4	
	200	85.4	475	109.0	
20 min.					
break	205	85.8	500	110.4	35 min.
	210	86.1	505	110.6	break
			515	110.9	
			545	112.8	
			565	114.7	End of run

TABLE 5a (Fig. 19)

C_3H_6 on untreated TiO_2 (B)

C_3H_6 - pressure = 40 mms.

Bourdon sensitivity = 0.018 (1) mm. div^{-1}

	t(mins)	Δp(divs)	t	Δp
	0	0	40	25.1
	0.5	3.2	50	31.3
	1	4.6	60	35.6
	3	6.6	70	39.5
	5	7.9	80	42.6
	10	9.5	90	45.1
	15	10.1	overnight break in illumination	
	20	9.9	91	43.9
	25	10.3	92	44.7
LIGHT (L)	30	10.6	95	45.7
	30.5	11.2	100	47.1
	31	13.1	115	49.8
	33	17.4	135	52.6
	35	20.3		

TABLE 5b (Fig. 19)

Repeat of 5a following 3 hrs. evacuation

C_3H_6 - pressure = 42.mm. Sensitivity = 0.018 (1) mm.div^{-1}

t(mins)	Δp(divs)		t	Δp
0	0	LIGHT (L)	30	12.4
0.5	3.0		30.5	10.4
1	4.2		31	10.8
3	6.9		32	11.4
5	7.9		35	12.3
10	10.0		40	13.5
15	10.9		45	14.7
20	11.6		50	15.6
25	12.2		60	17.5

TABLE 6 (Fig. 20)

Uptake of a C_3H_6/O_2 mixture on TiO_2 (A)

C_3H_6 - pressure = 42 mm. O_2 pressure = 14 mm.

Bourdon sensitivity = 0.018 (1) mm. div^{-1}

t(mins)	Δp(divs)		t	Δp
0	0		85.5	86.9
0.5	14.3		86	88.8
1	21.5		87	92.3
3	34.6		90	102.0
5	39.8		95	117.0
10	48.1		100	130.2
20	59.7	Light off(o)	105	142.7
35	70.1		106	143.8
50	77.6		110	144.2
70	82.9		115	144.4
LIGHT(L) 85	85.2			

TABLE 7 (Fig. 21)

C_3H_6/O_2 on untreated TiO_2 (A)

C_3H_6 pressure = 36 mm. O_2 pressure = 14 mm.

sensitivity = 0.018 (1) mm div^{-1}

	t(mins)	Δp(divs)	t	Δp	t	Δp
*	"0"	"0"(x)	32	14.6	86	-2.9
	1	1.0	35	12.5	87	+1.3
	5	4.6	40	9.8	90	11.2
	11	10.9	52	4.3	95	24.4
LIGHT OFF(o)	20	19.6	62	0.6	100	34.1
	20.5	20.5	70	-1.9	105	40.6
	21	20.0	85	-5.9		
	22	19.0	LIGHT ON(L)			
	25	17.2	85.5	-4.8		

* t = "0" signifies start of observation following overnight illumination. Likewise, 'Δp' is not known.

TABLE 8 (Fig. 22)

Derived Rate data for O_2 on TiO_2(B)

from Table 1

(Bourdon sensitivity = 0.050 (3) mm/div)

$\bar{q}$ (divs)	10/rate (20)*	Log_{10}Rate (20)*
2.4	1.1	0.97
5.7	2.6	0.58
7.3	3.6	0.45
8.6	4.2	0.38
10.2	5.0	0.30
12.0	6.7	0.18
13.4	7.7	0.11
14.6	9.1	$\bar{0}$.04
15.6	11.1	$\bar{1}$.95
16.5	11.1	$\bar{1}$.95
17.4	11.1	$\bar{1}$.95
18.2	12.5	$\bar{1}$.90
19.0	12.5	$\bar{1}$.90
19.8	14.3	$\bar{1}$.85
20.5	14.3	$\bar{1}$.85
21.2	14.3	$\bar{1}$.85
21.8	16.7	$\bar{1}$.78

* Rate (20) signifies the rate expressed as divs/20 mins

$$\text{i.e. Rate (20)} = 20\,\frac{dq}{dt}$$

TABLE 9 (Fig. 23A & B)

O_2 on untreated TiO_2 (A)

O_2 pressure = 48 mm.

Bourdon sensitivity = 0.021(4) mm/div.

t(mins)	Δp(divs)	$\bar{q}$(divs)	1/Rate(4)	$\log_{10}$ Rate(4)
0	0			
0.5	1.3	2.0	0.13	0.90
1	2.4	5.6	0.16	0.81
2	4.1	8.4	0.22	0.66
5	8.7	10.6	0.24	0.62
10	13.4	12.5	0.28	0.56
15	17.1	14.2	0.31	0.51
22	20.7	15.7	0.36	0.45
30	24.9	17.1	0.36	0.45
40	27.5	18.4	0.42	0.38
52	33.3	19.5	0.50	0.30
67	35.0	21.0	0.53	0.28
82	38.8	22.8	0.56	0.26
112	43.1	24.5	0.67	0.18
142	47.0	25.9	0.77	0.11
155	48.5	27.1	0.91	0.04
		28.2	0.83	0.08
		29.4	0.91	0.04

TABLE 10 (Fig. 24)

Derived rate data for C_2H_4 on TiO_2 (B)

from Table 2

(Bourdon sensitivity = 0.050(3) mm/div).

$\bar{q}$ (divs)	10/Rate (20)	$\log_{10}$ Rate (20)
2.0	0.6	1.22
4.8	1.8	0.75
5.9	3.1	0.51
6.7	3.6	0.45
7.5	5.6	0.26
8.4	5.6	0.26
9.2	6.3	0.20
9.9	8.3	0.08
10.5	10.0	0.00
11.0	10.0	0.00
11.4	12.5	$\bar{1}$.90
11.8	12.5	$\bar{1}$.90
12.3	14.3	$\bar{1}$.85
12.9	16.7	$\bar{1}$.78

TABLE 11a (Fig. 25 a)

Derived rate data for C_3H_6 dark uptake on TiO_2(B)

from Table 5B

(Bourdon sensitivity = 0.018 mm. div^{-1})

$\bar{q}$	1/Rate (1)	$\log_{10}$ Rate (1)
1.5	0.17	0.78
3.6	0.42	0.38
5.0	0.67	0.18
6.3	0.83	0.08
7.3	1.4	$\bar{1}$.85
7.9	2.0	$\bar{1}$.70
9.0	2.8	$\bar{1}$.56
10.4	5.0	$\bar{1}$.30
11.3	6.3	$\bar{1}$.20
12.0	10.0	$\bar{1}$.00
12.3	25.0	$\bar{2}$.60

TABLE 11b (Fig. 25B)

Derived rate data for C_3H_6 photoadsorption on TiO_2(B)

from Table 5A

(Sensitivity = 0.018 mm div^{-1})

$\bar{q}$	1/Rate (1)	$\log_{10}$ Rate (1)
2.5	0.40	0.39
6.7	0.55	0.24
9.6	0.83	0.08
11.8	1.0	$\bar{0}$.00
13.7	1.2	$\bar{1}$.93
16.3	1.4	$\bar{1}$.85
19.4	1.85	$\bar{1}$.73
21.8	2.3	$\bar{1}$.64
24.0	2.4	$\bar{1}$.62
26.9	2.6	$\bar{1}$.58
30.4	3.1	$\bar{1}$.51
33.3	4.0	$\bar{1}$.40

TABLE 12 (Fig. 26)

Effect of pressure on O_2-uptake on TiO_2 (B)

Bourdon sensitivity = 0.050(3)mm/div.

P (mm.)	t (mins)	Δp (divs.)
23.5	0	0
	0.5	0.5
	1	0.8
	3	1.7
	5	2.4
	7	3.1
	10	3.8
	14	4.6
	(15)	(4.85)
32.7	16	5.05
	18	5.35
	20	5.75
	25	6.45
	29	7.05
	(30)	(7.15)
42.2	31	7.25
	33	7.55
	36	7.85
	41	8.45
	45	8.75
15 min. break in illumination.		
86.5	46	8.85
	50	9.15
	55	9.45
	61	9.85
$1\frac{3}{4}$hr. break in illumination		
118.7	61.5	9.65
	62	9.75
	64	9.95
	70	10.35
	77	10.55
	82	10.85
	88	10.95
	96	11.15
End of run		

(n).....extrapolated values.

TABLE 13 (Fig.27)

Derived rate data for O_2 on TiO_2 (B)
with two pressure-increases, from Table 12.

(Bourdon sensitivity = 0.050(3)mm/div.)

$\bar{q}$ (divs.)	$^1/_{\text{Rate}}$ (l)
0.40	1.3
1.05	2.0
1.70	2.6
2.40	2.9
3.05	3.5
3.55	4.2
4.35	4.8
5.25	6.0
6.05	6.5
6.80	7.1
7.50	7.7
8.10	9.1
8.55	12.5

(Pressure increases at q = 4.85 and
at q = 7.15)

TABLE 14 (Fig.28)

Effect of pressure on C_2H_4 uptake on TiO_2 (B)

Bourdon sensitivity = 0.050(3)mm/div.

P (mm.)	t (mins.)	Δp (divs.)	P	t	Δp
20.5	0	0	100.6	27	6.2
	0.5	1.0		30	6.5
	1	1.4		36	7.2
	2	1.9		40	7.7
	3	2.2		45	8.0
	4	2.5		50	8.5
	(5)	(2.75)		55	8.8
32.6	6	3.1o		60	9.2
	8	3.5o			
	10	3.8			
	12	4.1			
	14	4.3			
	(15)	(4.40)			
67.6	16	4.7			
	18	5.1			
	20	5.3			
	24	5.7			
	(25)	(5.80)			

(n).....extrapolated value.

TABLE 15A (Fig. 30A)

Effect of pressure on C_3H_6 dark uptake on TiO_2 (B)

Bourdon sensitivity = 0.050(3) mm/div.

P(mm)	t(mins)	Δp(divs)	P	t	Δp
25.8	0	0		20	3.0
	0.5	0.6		(21)	(3.05)
	1	0.9	108.4	22	3.55
	3	1.3		25	3.95
	5	1.6		30	4.35
	7	1.8		35	4.45
	9	1.8		40	4.75
	(10)	(1.9)			
50.7	11	2.2		End of run	
	13	2.5			
	15	2.7			
	17.5	2.9			

TABLE 15B (Fig. 30B)

Effect of pressure on C_3H_6 light uptake on TiO_2(B)

Bourdon sensitivity = 0.050(3) mm/div.

P(mm)	t(mins)	Δp(divs)	P	t	Δp
24.2	0	0		19	3.6
	1	0.6		(20)	(3.65)
	3	1.0	108.5	21	4.25
	5	1.3		25	4.95
	7	1.6		30	5.65
	9	1.9		40	6.45
	(10)	(2.0)		44	6.85
52.3	11	2.3		(45)	(6.90)
			45.1	46	6.4
	13	2.7		47	6.2
	15	3.2		50	6.2
	17	3.3		60	6.4

TABLE 16 (Fig. 31)

Effect of C_3H_6 pressure on

Dark uptake of a C_3H_6/O_2 Mixture on TiO_2 (B)

Bourdon sensitivity = 0.050(3) mm/div.

O_2 pressure = 23.6 mm. (constant).

C_3H_6 P(mm)	t(mins)	Δp(divs)
20.5	0	0
	0.5	4.7
	1	6.2
	2	7.1
	3	7.4
	5	7.6
	7	7.7
	9	7.8
	(10)	(7.9)
47.3	10.5	12.1
	11	14.2
	12	16.3
	15	17.9
	20	18.6
	24	19.0
	(25)	(19.0)
70.9	25.5	20.6
	26	21.5
	28	23.0
	30	23.5
	35	24.3
	39	24.6
	(40)	(24.6)
88.7	41	25.5
	42	25.9
	45	26.8
	55	28.0
	60	28.1

TABLE 17

Derived rate data for C_2H_4 and C_3H_6 uptakes

from Tables 14 & 15A (Figs 28 & 30A)

Uptake	b/a	Pb/Pa	Initial $\frac{\text{Rate b}}{\text{Rate a}}$	$\bar{q}_a/\bar{q}_b$	x
C_2H_4 photo -	2/1	$^{32.6}/_{20.5} = 1.59$	$^{0.35}/_{1.4} = 0.25$	$^{0.7}/_{2.9} = 0.24$	0.09
	3/2	$^{67.6}/_{32.6} = 2.08$	$^{0.25}/_{0.35} = 0.71$	$^{2.9}/_{4.5} = 0.65$	0.13
	4/3	$^{100.6}/_{67.6} = 1.49$	$^{0.20}/_{0.25} = 0.80$	$^{4.5}/_{5.9} = 0.76$	0.12
	3/1	$^{67.6}/_{20.5} = 3.30$	$^{0.25}/_{1.40} = 0.18$	$^{0.7}/_{4.5} = 0.66$	0.12
	4/2	$^{100.6}/_{32.6} = 3.10$	$^{0.20}/_{0.35} = 0.57$	$^{2.9}/_{5.9} = 0.49$	0.13
	4/1	$^{100.6}/_{20.5} = 4.91$	$^{0.20}/_{1.40} = 0.14$	$^{0.7}/_{5.9} = 0.12$	0.11
					$\bar{x} = 0.12$
C_3H_6 dark -	2/1	$^{50.7}/_{25.8} = 1.97$	$^{0.30}/_{0.90} = 0.33$	$^{0.45}/_{2.05} = 0.22$	0.61
	3/2	$^{108.4}/_{50.7} = 2.14$	$^{0.50}/_{0.30} = 1.67$	$^{2.05}/_{3.80} = 0.54$	1.48
	3/1	$^{108.4}/_{25.8} = 4.20$	$^{0.50}/_{0.90} = 0.56$	$^{0.45}/_{3.80} = 0.12$	1.07
					$\bar{X} = 1.05$

$$x = \log \left(\frac{\text{Rate b}}{\text{Rate a}} \cdot \frac{\bar{q}b}{\bar{q}a} \right) / \log \frac{Pb}{Pa}$$

TABLE 18

Uptake of O_2 on pre-illuminated TiO_2 (A)

O_2 Pressure = 36 mm.

Bourdon sensitivity = 0.0237 mm.div^{-1} Pre-illumination = $18\frac{1}{2}$ hrs.

t(mins)	Δp(divs)	$\bar{q}$(divs)	^{1}/Rate(1)	$\text{Log}_{10}{}^{\text{Rate}}$(1)
0	0	3.2	0.8	$\bar{0}.10$
1	1.8	8.5	1.2	$\bar{1}.94$
3	4.0	12.5	1.4	$\bar{1}.86$
5	6.6	15.8	1.7	$\bar{1}.76$
10	11.3	18.6	1.9	$\bar{1}.73$
20	17.7	21.0	2.3	$\bar{1}.62$
30	22.6	24.0	2.5	$\bar{1}.60$
40	25.8	27.7	3.1	$\bar{1}.52$
50	29.2	30.9	3.2	$\bar{1}.50$
60	32.3	34.2	3.1	$\bar{1}.52$
70	34.4	36.5	4.0	$\bar{1}.40$
92	40.7	38.9	4.3	$\bar{1}.36$
107	43.6	41.1	4.5	$\bar{1}.33$
122	46.2	44.2	5.0	1.30
137	49.2	47.8	5.8	$\bar{1}.23$
167	52.4	50.9	7.2	$\bar{1}.15$
182	54.6	53.5	7.7	$\bar{1}.11$
200	56.8	56.0	8.4	$\bar{1}.08$
227	59.8	58.3	8.4	$\bar{1}.08$
257	62.6	60.3	10.5	$\bar{2}.98$
287	65.2			
302	66.5			
325	68.2			

TABLE 19

Uptake of C_2H_4 on pre-illuminated TiO_2 (A)

C_2H_4 pressure = 53 mm.

Bourdon sensitivity = 0.0237 mm.div.$^{-1}$

Pre-illumination = $18\frac{1}{2}$ hrs.

t(mins.)	Δp(div.)	$\bar{q}$(divs.)	^{1}/Rate(1)	Log.$_{10}$Rate(1)
0	0	8.5	0.3	0.53
1	6.5	20.0	0.9	$\bar{1}$.98
3	13.1	25.2	1.6	$\bar{1}$.80
5	17.1	31.3	2.6	$\bar{1}$.59
7	19.7	34.4	4.0	$\bar{1}$.40
10	23.2	36.9	4.4	$\bar{1}$.36
12	24.7			
15	26.6	38.9	5.9	$\bar{1}$.23
20	29.5	40.3	9.1	$\bar{1}$.04
37	35.1	41.4	11.1	$\bar{2}$.95
45	37.2	42.2	11.1	$\bar{2}$.95
60	39.7	43.0	14.3	$\bar{2}$.85
67	40.0			
82	42.0	43.6	20.0	$\bar{2}$.70
97	43.5	44.2	20.0	$\bar{2}$.70
112	43.9			
130	44.6			

TABLE 20 (Fig.34)

Effect of pre-illumination and O_2-treatment on C_2H_4 uptake on TiO_2 (A)

Bourdon sensitivity = 0.024 mm.div.$^{-1}$

Initial C_2H_4-pressure = 50.5 mm.

t(mins.)	Δp (divs.)
0	0
0.5	1.2
1	2.0
2	3.2
5	5.1
10	7.6
15	9.4
25	11.3
(A) Overnight illum. in vacuo + dark stand for 1hr. New C_2H_4 -P=51.5mm.	
25.5	10.6
26	10.6
27	10.5
30	10.8
35	10.9
40	11.3
(B) O_2 photoadsorbed for 125 mins. New C_2H_4-P=47mm.	
40.5	12.1
41	12.5
43	13.8
45	14.4
50	15.8
55	16.9

t	Δp
(C) Overnight illum. in vacuo + dark stand for 1hr. New C_2H_4 -P=52 mm..	
55.5	16.7
56	16.7
57	16.8
60	16.9
70	17.9
80	18.9
90	19.0
115	20.0
(D) O_2 photosorbed for 4 hrs. Overnight illum. in vacuo + 1 hr. dark stand. New C_2H_4-P=49mm.	
116	19.0
117	19.2
120	20.0
125	21.0
130	21.6
135	22.9
140	23.4

TABLE 21 (Fig. 35)

Effect of pre-illumination and dark O_2-treatment on C_2H_4 uptake on TiO_2 (A)

Bourdon sensitivity = 0.024 mm.div.$^{-1}$

Initial C_2H_4-pressure = 49 mm.

t(mins.)	Δp (divs.)
0	0
0.5	2.1
1	3.2
2	3.5
5	6.0
10	7.5
15	9.1
(O) Film pumped over week-end New C_2H_4-P=54mms.	
15.5	9.9
16	10.3
17	10.6
20	11.3
25	12.5
30	13.0
(P) 3hrs.40mins.illum. in vacuo + 40 mins.dark stand. New C_2H_4-P=53mm.	
30.5	12.5
31	12.6
35	12.7
40	13.0
50	13.6
55	13.7

t	Δp
(Q) Overnight stand in 9.5 mms. O_2 + 3 hours pumping. New C_2H_4-P=50.5 mm.	
55.5	13.9
56	14.5
57	14.8
60	15.1
65	15.6
71	16.4
77	16.9

TABLE 22 (Fig. 36)

Effect of illumination in vacuo on C_2H_4 uptake on NH_3 - treated TiO_2 (A)

Pre-treatment:- 4 hrs in 23 mm. NH_3 followed by overnight pumping.

Initial C_2H_4 - pressure = 49 mm.

Bourdon sensitivity = 0.050(3) mm. $div.^{-1}$

t(mins)	Δp(divs)
0	0
0.5	0.6
1	0.9
2	1.2
5	1.9
10	2.8
15	3.5
26	4.9
35	5.8
45	6.7
Overnight illum^{n}. in vacuo + 1 hr. dark pumping New C_2H_4 P = 46 mm.	
45.5	7.3
46	7.9
47	8.8
50	10.8
55	13.0
65	16.1
75	18.3
85	20.3
90	21.2
$4\frac{1}{2}$ hrs illum^{n}. in vacuo + overnight dark pumping New C_2H_4 P = 46 mm.	
91	21.4
92	21.6
95	22.1
100	23.0
111	24.9
115	25.4
125	26.7
130	27.3

TABLE 23

Uptake of NO on TiO_2 (B)

Pressure = 33.0 mm.

Bourdon sensitivity = 0.050(3) mm.div^{-1}

	t(mins)	Δp(divs)	$\overline{\Delta p}$(divs)	^{1}/Rate(min div^{-1})	$\log_{10}$ Rate
	0	0	4.3	0.29	0.53
	0.5	0.4	11.8	0.37	0.43
	3	0.7	20.2	0.51	0.29
	10	0.7	29.2	0.63	0.20
LIGHT	0	0	36.3	0.73	0.13
ON	0.5	2.1	45.7	0.83	0.08
	1	3.9	56.7	1.05	$\bar{1}$.98
	3	10.0	65.6	1.15	$\bar{1}$.94
	5	15.1	73.5	1.43	$\bar{1}$.85
	7	19.2	80.4	1.49	$\bar{1}$.83
	10	24.9			
	15	32.9			
	20	39.9			
	30	51.6			
	40	61.3			
	50	69.8			
	60	77.1			
	75	86.9			
	85	93.2			
	95	98.6			
	100	101.4			

TABLE 24

Variation of C_2H_4 uptake with time on pre-treated films (TiO_2 B)

C_2H_4 pressures ~ 50 mm.

Bourdon sensitivity 0.050(3) mm.div^{-1}

t(mins) *	Untreated (1)	NOtreated (2)	O_2 - treated (3)	Pre-illuminated (4)	$(1)/(2)$	$(1)/(4)$	$(3)/(1)$
$\frac{1}{2}$	1.0	0	1.7	0.1		10.0	1.7
2	2.2	0.1	4.4	0.4	22	5.5	2.0
5	3.3	0.4	7.5	0.8	8.3	4.1	2.3
10	4.5	0.6	10.2	1.3	7.5	3.5	2.3
25	6.3	-	14.0		-		2.2
45	8.0	2.2	16.2		3.6		2.0
60	9.0	3.0	17.5		3.0		1.9

BIBLIOGRAPHY

1. JACOBSEN, Ind. Eng. Chem. 41, 523 (1949).

2. KENNEDY, Ph.D. Thesis, Edinburgh (1956).

3. McLEAN, " " , " (1959).

4. McLINTOCK, " " , " (1963).

5. CRONEMEYER and GILLEO, Phys.Rev. 82, 975 (1951).

6. " " " , ibid. 87, 876 (1952).

7. GOODEVE, Trans. Farad. Soc., 33, 340 (1937).

8. WEYL & FORLAND, Ind. Eng. Chem. 42, 257 (1950).

9. GOODEVE and KITCHENER, Trans.Farad.Soc., 34, 902 (1938).

10. EGERTON, J. Soc. Dyers & Colourists, 65, 764 (1949).

11. MacKENZIE, Ph.D. Thesis, Edinburgh (1952).

12. McTAGGART & BEAR, J.Appl. Chem. 8, 72 (1958)

13. KENNEDY, RITCHIE and MacKENZIE, Trans.Farad.Soc. 54, 119 (1958).

14. McLEAN & RITCHIE, J.Appl.Chem. 15, 452 (1965).

15. McLINTOCK & RITCHIE, Trans.Farad.Soc. 61, 1007 (1965)

16. KENNEDY, unpublished results, University of Edinburgh.

17. BEWS, Ph.D. Thesis, Edinburgh (1964).

18. C.A.53, 9818e (1959); FILIMONOV, Optika i Spekt., 5, 709 (1958).

19. VICKERMAN, unpublished results, University of Edinburgh.

20. ASHER & GREGG, J. Chem.Soc., 5057 (1960).

21. CHESSICK & ZETTLEMOYER, Adv.Catal. 11, 263 (1959).

22. YATES, J. Phys.Chem. 65, 746 (1961).

23. REYERSON & HONIG, J.A.C.S. 75, 3920 (1953).

24. C.A. 57, 8095 i (1962); RAPOPORT & SOLONITSYN, Dokl. Akad. Nauk. S.S.S.R. 143, 1149 (1962).

25. STONE, Adv. Catal. 13, 1 (1962).

26. GOPALO RAO, Z. Phys.Chem. 184A, 377 (1939).

27. GOPALO RAO & MURTY, J.Ind.Chem.Soc., 12, 127 (1941).

28. SCHURZ & KIENZL, Fraserforschung U. Textiltechnik, 12, 513 (1958).

29. SCHURZ & KIENZL, Svensk. Papperstidning 61, 844 (1958).

30. GOETZ & INN, Rev. Mod. Phys. 20, 131 (1948).

31. FÖRLAND, Int.Symp. on React. of Solids, Gothenburg, 1952.

32. CLARK & VONDJIDIS, J. of Catal. 4, 691 (1965).

33. HABER & STONE, Trans. Farad.Soc. 59, 192 (1963).

34. TERENIN & SOLONITSYN, Disc. Farad.Soc. 28, 28 (1959).

35. KOBAYASKI & KAWAJI, J. Chem.Phys. 25, 907 (1956).

36. C.A. 52, 16898 d.; SOLONITSYN, Zhur.Fiz. Khim. 32, 1241 (1958).

37. SCHWAB, Adv. in Catal. 9, 229 (1957).

38. GRAY & SAVAGE, Disc. Farad.Soc. 28, 159 (1959).

39. SHOCKLEY, Phys. Rev. 56, 317 (1939).

40. STATZ, DE MARS, L. DAVIS JUN. and A. ADAMS Jun. "Semiconductor Surface Physics," Ed. Kingston, O.U.P. (1957).

41. C.A. 64, 4348 f (1966); SUITO & SHIOJIRI.

42. GRANT, Rev. Mod. Phys. 31, 646 (1959).

43. CONN, HUMPHREY, MAGEE & WALLACE, J. Am. Pharm. Assoc., Sci.Ed., 1956, 46, 311.

44. ANDERSON, COLLEN, KUYLENSTIERNA & MAGNELI, Acta. Chem. Scand. 11, 1641 (1957).

45. HURLEN, ibid. 13, 365 (1959).

46. FREDERIKSE, J. Appl. Phys. 32, 2211 (1961).

47. CHESTER, ibid. 32, 2233 (1961).

48. GRAY, McCAIN & MASSE, J. Phys.Chem. 63, 472 (1959).

49. EARLE, Phys. Rev. 61, 56 (1942).

50. EHRLICH, Z. Electrochem. 45, 362 (1939).

51. CRONEMEYER, Phys. Rev. 113, 1222 (1959).

52. BRECKENRIDGE,& HOSLER, ibid., 91, 793 (1953).

53. MOTT & GURNEY, Electronic Processes in Ionic Crystals, O.U.P. (1940).

54. BEVAN, DAWES & FORD, Private Communication.

55. YOUNG, SHUSTUS & GILLIAM, Bull Am.Phys. Soc. 6, 248,(1959)

56. Science Abstracts (Physics) 65, 10374; SRIVISTAVA, Physica (Netherlands) 28, 268 (1962).

57. JOHNSON & WEYL, J. Am.Ceram. Soc. 32, 398 (1949).

58. MANN (Former British Rayon Research Assocn), Private Communication (1956).

59. SANDLER,J. Phys. Chem. 58, 54 (1954).

60. BERANEK, BARTON, SEKERKA & SMRCEK, Collection Czechoslav.Chem. Commun. 25, 358-374 (1960).

61. LEWIS & PARFITT, Trans. Farad.Soc. 62, 204 (1966).

62. GREGG, "Chemisorption," Proc.Symp., Keele Univ. (1956), P.68 (Butterworths).

63. LATTY, J. Appl. Chem. 8, 96 (1958).

64. TAYLOR & LIANG, J.A.C.S. 69, 1306 (1947).

65. HOLLABAUGH & CHESSICK. J.Phys.Chem., 65, 109 (1961).

66. GEBHARDT and HERRINGTON, J. Phys.Chem., 62, 120 (1958).

67. MELNICK, J. Chem.Phys. 26, 1136 (1957).

68. C.A. 56, 9567 e; IZVOZCHIKOV, Fiz. Tverdogo Tela 3, 3229 (1961).

69. WOODS & WRIGHT, Solid State Phys. in Electronics and Telecommuns. Proc. Int. Conf. (Brussels, 1958).

70. BUBE, "Photo-conductivity of Solids", Wiley & Sons Inc., N.Y. (1960).

71. BARRY & KLIER, Disc. Farad. Soc. 31, 219 (1961).

72. CLARK & BERETS, Adv. in Catal. 9, 204 (1957).

73. EMMETT Ed., Catalysis 7 (1960) (Reinhold, N.Y.)

74. WAGNER, Z. Phys.Chem. B21, 25 (1933) and B32, 447 (1936).

75. MORRISON, Adv. in Catal. 7, 259 (1955).

76. HAYWARD & TRAPNELL, "Chemisorption", Butterworths (1964).

77. MACFARLANE, Unpub'd results, University of Edinburgh (1963).

78. GRIFFITH & MARSH, "Contact Catalysis", O.U.P. (1957).

79. WOLKENSTEIN, Adv. in Catal. 12, 189 (1960).

80. WEISER & MILLIGAN, J. Phys.Chem. 38, 513 (1934).

81. GREGORY, Unpub'd results, University of Edinburgh.

82. FEIGL, Spot Tests: Organic Applications, P. 241.

83. YATES & LUCCHESI, JACS 86, 4258 (1964).

84. ROMERO-ROSSI & STONE, Unpub'd results (1961) see (25).

85. SMITH & METZNER, J. Phys. Chem. Vol.68, 10, 64 (2741).

86. ANDERSON, Tilden Lecture, 1953.

87. CHARMAN et al., Trans. Farad.Soc. 59, 453 (1963).

88. ENGEL and HAUFFE, Z. Electrochem. 57, 762 (1953).

89. WEISZ, J. Chem. Phys. 21, 1531 (1953).

90. HESLOP & ROBINSON, Ed. "Inorganic Chemistry," Elsevier, 1960.

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